NASA CONTRACTOR REPORT

NASA CR-1371

NASA CR-1371

SOLUBILITY OF REFRACTORY METALS AND ALLOYS IN POTASSIUM AND IN LITHIUM

by R. L. Eichelberger, R. L. McKisson, and B. G. Johnson

Prepared by
NORTH AMERICAN ROCKWELL CORPORATION
Canoga Park, Calif.
for Lewis Research Center

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • MAY 1969

NASA CR-1371

SOLUBILITY OF REFRACTORY METALS AND ALLOYS IN POTASSIUM AND IN LITHIUM

By R. L. Eichelberger, R. L. McKisson, and B. G. Johnson

Prepared under Contract No. NAS 3-8507 by
ATOMICS INTERNATIONAL
North American Rockwell Corporation
Canoga Park, Calif.

for Lewis Research Center

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

FOREWORD

The work described herein, which was conducted by Atomics International, a Division of North American Rockwell Corporation, was performed under NASA Contract NAS3-8507. The Project Manager for NASA was Mr. Russell A. Lindberg, Space Power Systems Division, NASA-Lewis Research Center, Cleveland, Ohio. The report was originally issued as Atomics International Report AI-68-110.

ABSTRACT

The solubilities of several pure metals and alloys in liquid potassium and lithium were studied as follows: In K, Ta from the alloys T-111*, ASTAR-811C*, and Ta-0.5Zr; Nb from the alloys Cb-1Zr and Nb-0.5Zr; Mo from the alloys Mo-0.5Zr and TZM*; Hf, Zr, W, and Re from pure metals; in Li, Ta from the alloys T-111* and ASTAR-811C*; Hf from ASTAR-811C* and pure hafnium; and Mo, W, and Re from the pure metals. The solvent metals were purified by distillation, and were of exceptional purity.

All operations in which there might be danger of contamination of the high purity materials were carried out in high vacuum (pressure $< 10^{-6}$ Torr) in a complex of interconnected vacuum chambers.

Apparent solubilities at 1200°C for the systems studied are as follows:

	wppm in K	wppm in Li
Ta from T-111*	7	1 - 3
Ta from ASTAR-811C*	7	1 - 3
Ta from Ta-0.5Zr	500	
Nb from Cb-1Zr	6	
Nb from Nb-0.5Zr	10	
Mo from Mo-0.5Zr	100	
Mo from TZM*	8	
Hf from ASTAR-811C*		8
Hf (zone refined)	100	6
Zr (zone refined)	80	
W (vapor deposited)	40	2
Re	< 1	1
Mo		5

The data are generally too sparse and scattered to assign a definite temperature dependence. The results show conclusively, however, that the presence of a gettering element (Zr, Hf, Ti) in a refractory metal very substantially reduces its apparent solubility, and that about 2% by weight of the getter is needed to provide apparent solubilities under 10 wppm. The solubility in lithium is significantly less than in potassium, possibly because of the oxygen gettering ability of the lithium itself.

* Alloy Compositions

T-111:	Ta - 8W - 2Hf
ASTAR-811C:	Ta - 8W - 1 Re - 1 Hf - 0.025C
TZM:	Mo - 0.5 Ti - 0.07 Zr

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

SUMMARY

To increase the amount of reliable information on the apparent solubilities of refractory containment metals for liquid metals at high temperatures, solubility experiments were carried out with liquid potassium and lithium, using a number of refractory metal alloys and pure metals. The solute-solvent systems investigated were T-111 (Ta-8W-2Hf), ASTAR-811C (Ta-8W-1Re-1Hf-0.025C), Ta-0.5Zr, Cb*-1Zr, Nb*-0.5Zr, Mo-0.5Zr, TZM (Mo-0.5 Ti-0.07Zr), Hf, Zr, W, and Re in potassium, and T-111 (Ta-8W-2Hf), ASTAR-811C (Ta-8W-1Re-1Hf-0.025C), Hf, Mo, W, and Re in lithium.

The experimental method used emphasized the purity of both solute and solvent metals, except in the case of commercial alloys. The solvents potassium and lithium were prepared by gettering and subsequent distillation. The components for a solubility experiment were assembled, loaded with liquid metal, and electron-beam welded into a vacuum-tight assembly in high vacuum chambers. The pressures in the chambers were less than 10^{-6} Torr, except when gas released during the welding operation caused a decade rise in pressure. The experimental assembly consisted of a solute crucible, a sample collector of a different refractory metal, and an outer capsule of molybdenum or T-222 (Ta-10W-2Hf) alloy. The liquid metal was loaded into the crucible after the crucible was welded to the sample collector. Then the collector was closed by welding a cap on it. This assembly was finally enclosed in a welded outer capsule. During a solubility equilibration, the solvent remained in the sample crucible, but at the end of the desired time the whole assembly was rotated about a horizontal axis out of the furnace, and the solvent transferred to the sample collector. High vacuum manipulators were used to perform the necessary operations in the vacuum systems.

A major problem was encountered when the work with lithium solvent was begun. Because of the combination of the high surface tension and the low density of lithium, it was not possible to carry out the transfer of solvent from crucible to collector by a simple inversion of the assembly. The problem was solved by installing a tungsten (or tantalum) wire along the inside wall of the crucible-collector assembly, to break the surface of the lithium and provide a capillary path for it to flow down.

Other concerns affecting the validity of the experimental results included the possibility that solute material had vaporized from the crucible onto the collector walls during a welding operation, and that solute atoms might diffuse far enough into the collector after transfer (by grain boundary diffusion) that it would not be removed by the etching procedure used by the analytical chemist. The first of these problems was overcome by physically removing a layer of surface from the inside of the collector by machining after the weld was made. Careful analyses of successive skin cuts from the inside of both used and unused collectors showed that the second problem did not exist.

*The symbol "Cb" is used in this report for columbium (niobium) where it is a constituent of a commercial alloy. The symbol "Nb" is used for the pure metal, or where it is a constituent of a special alloy.

For 13 of the 18 systems studied, four or fewer data points were taken, and for all systems the scatter which seems to be inherent in this kind of experiment was found to be present. Therefore, the only system for which the data permit a calculation of a heat of solution is T-111 alloy (Ta-8W-2Hf) in potassium. The heat of solution of tantalum from this alloy is about 9600 calories per mole.

Although the sparseness and scatter of data did not warrant an exhaustive treatment of the data, a number of important conclusions can be drawn from the results of these experiments. The addition of a gettering element (Zr, Hf, or Ti) to the refractory metals tantalum and niobium dramatically reduces the apparent solubility of the metal in potassium or lithium. The reduction in solubility was found to be a function of the amount of getter in the 0 - 2 weight percent range, but it seems doubtful that greater additions would reduce the apparent solubility more. Except for rhenium, whose solubility is just at the limit of analytical chemistry detection, all solutes are more soluble in potassium than in lithium at a given temperature. Table I summarizes the results of the experimental program.

TABLE I

Summary of Results of the Experimental Program

Solute	Solubility, wppm in K	Temp. Range	Solubility wppm in Li	Temp. Range
Ta from T-111*	$\log_{10} S(\text{wppm}) = 2.099 - \frac{2090}{T(°K)}$	1200-1600	0 - 3	1200-1600
Ta from ASTAR-811C*	6 - 10	1200-1600	0 - 3	1200-1600
Ta from Ta-0.5Zr	500 - 3000	1200-1600		
Nb from Cb-1Zr	~ 6	1200-1400		
Nb from Nb-0.5Zr	10 - 15	1200-1600		
Mo from Mo-0.5Zr	~ 100	1200-1400		
Mo from TZM*	~ 12	1400		
Hf from ASTR-811C*			6 - 10	1200-1600
Hf (zone refined)	~ 100		~ 6	1000-1400
Zr (zone refined)	60 - 100	900-1200		
W (vapor deposited)	40 - 80	1200-1600	0 - 3	1200-1600
Re	< 1	1200-1600	0 - 2	1200-1600
Mo			2 - 15	1200-1600

* T-111: Ta-8W-2Hf

ASTAR-811C: Ta-8W-1Hf-1Re-0.025C

TZM: Mo-0.5Ti-0.07Zr

INTRODUCTION

The work reported here is a continuation and extension of work with high purity potassium solvent previously reported from this laboratory (20). The purpose of the work was to obtain solubility information from selected solid metal-liquid metal systems of interest for possible application in high temperature liquid metal heat transfer equipment.

In the previous work, it was found that the apparent solubility of niobium (columbium) from a Cb-1Zr alloy solute was about one tenth that of niobium from a triple-pass zone-refined single crystal solute (20). Similar results have been noted in other laboratories in that gettered alloys in sealed alkali metal capsules and loops have almost invariably shown lower corrosion rates than have the corresponding ungettered materials. As a result of this sort of observation, the suggestion has been made that the gettered alloys show low metal solubilities because their effective oxygen contents are very low, and that even a few ppm oxygen such as is found in highly purified pure metals is enough to cause an appreciable increase in the apparent solubility of the metal. That oxygen may play such a role is perhaps exemplified by a comparison of the apparent solubilities of iron in potassium as measured by three laboratories. Table II shows the measured values at 1000 °C for three purity levels of iron. Although one cannot be certain that the variation in oxygen content of the iron is the only cause of the differences, it cannot be discounted as a very likely cause.

TABLE II

Comparison of Iron Solubility Values in
Potassium at 1000 °C

Description	O Content of Fe	O Content of K	Observed Solubility, ppm	Reference
"Armco"	510	20	1000	(25)
"Puron"	400	9 - 22	380	(8)
Triple-pass Zone-refined	< 8	14	115	(20)

If, then, the oxygen content of the solute metal does play a major or controlling role in the observed solubilities, the presence of a modest amount of a strong oxygen gettering metal should markedly reduce the observed solubilities of refractory metals. The testing of this thesis was one of the immediate goals of the work reported here. In the present study, the equilibrium concentration of several refractory metals in potassium and lithium in contact with pure metals and alloys was measured. A major emphasis was on alloys containing oxygen-gettering constituents (Zr, Hf, Ti), as is seen in the following list of the systems which were investigated.

In potassium: Tantalum from T-111*
Tantalum from ASTAR-811C
Tantalum from Ta-0.5 Zr
Niobium from Cb-1Zr
Niobium from Nb-0.5Zr
Molybdenum from Mo-0.5Zr
Molybdenum from TZM
Hafnium from pure hafnium
Zirconium from pure zirconium
Tungsten from pure tungsten
Rhenium from pure rhenium

In lithium: Tantalum from T-111
Tantalum from ASTAR-811C
Hafnium from ASTAR-811C
Hafnium from pure hafnium
Molybdenum from pure molybdenum
Tungsten from pure tungsten
Rhenium from pure rhenium

Solubility experiments with the refractory metals listed above have been carried out in liquid potassium at three laboratories, Pratt and Whitney (CANEL) (3,14), Douglas Aircraft (8), and Atomics International (20). Table III shows the results published by these laboratories, for solubility experiments with groups IV, V and VI elements in potassium. Table IV similarly shows the solubilities reported for elements from these groups in liquid lithium.

The data reported in Tables III and IV are notable for two major characteristics: Their sparseness and their diversity. Factors which contribute to the rather large scatter in most sets of data, and the frequent lack of agreement among laboratories, include the impurity level in solute and solvent, variability in sampling technique, and difficulty in the analytical chemistry of these systems at low solute concentrations. The present work is designed to minimize the uncertainties mentioned, but has not eliminated them, as discussed in this report. However, it has been possible to make some generalizations concerning solubilities in liquid potassium and lithium for metals of groups IV, V, and VI, using the data from Tables III and IV and the new information developed during the course of the work reported here. These generalizations are included in a later section of this report.

---

*Compositions and sources for the various materials are given in Table V.

TABLE III

Solubility of Selected Elements in Potassium

Solute	T, °C	Oxygen Content of K	Material	Container Material	Solubility wppm	Reference
Nb	1095	500	Nb	Cb-1Zr	7-48	3
	1095	1000	Nb	Cb-1Zr	12-72	3
	1095	3000	Nb	Cb-1Zr	14-72	3
	1095	5000	Nb	Cb-1Zr	2400-7200	3
	1000	3.5 -14	Nb	Nb	15-171	20
	1000	3.5	Cb-1Zr	Cb-1Zr	< 1	20
	1200	3.5 -14	Nb	Nb	17-72	20
	1200	3.5	Cb-1Zr	Cb-1Zr	6	20
	1225	9	Nb	Nb	1-3	8
	1275	9	Nb	Nb	7-12	8
	1340	9	Nb	Nb	6-11	8
	1375	9	Nb	Nb	13	8
Mo	1000	14	Mo	Mo	3.2-4.3	20
	1100	14	Mo	Mo	1.3-13	20
	1200	14	Mo	Mo	13.1-13.9	20
Ta	800	3.5	Ta	Ta	413	20
	900	3.5	Ta	Ta	572	20
	1000	3.5 -14	Ta	Ta	371-2730	20
	1100	14	Ta	Ta	688-2290	20
	1200	14	Ta	Ta	1550-2880	20
	1225	9	Ta	Ta	9	8
	1275	9	Ta	Ta	8-19	8
	1330	9	Ta	Ta	52-64	8
	1340	9	Ta	Ta	58-88	8
	1345	9	Ta	Ta	10-806	8
Ti	1200	9	Ti	Ti	61-100	8
	1300	9	Ti	Ti	45-134	8
Zr	1200	9	Zr	Zr	39-110	8
	1300	9	Zr	Zr	76, 77	8

TABLE IV

Solubility of Selected Elements in Lithium

Solute	T, °C	Oxygen Content of Li	Source Material	Container Material	Solubility, wppm	Reference
Cr	500	2400	Cr	Fe	90	13
	600				11	14
	675		Cr		15	17
	715	2400	Cr	Fe	130	13
	800		Cr	Fe	1000	2
	800				50	14
	925		Cr		90	17
	990	2400	Cr	Fe	430	13
	1000		Cr	Fe	11000	2
	1000				140	14
	1200		Cr	Fe	40000	2
	1200				295	14
Mo	550	2400	Mo	Fe	< 15	13
	665		Mo		7	17
	800				10	14
	860	2400		Fe	< 25	13
	925		Mo		15	17
	985	2400	Mo	Fe	140	13
	1000		Mo		1	6
	1000				< 1	4,5
	1000				19	14
	1200				300-1000	5
	1200				34	14
Nb	500	2400	Nb	Fe	< 30	13
	735	2400	Nb	Fe	80	13
	760		Nb	Mo	26	3
	800		Nb	Mo	21	3
	975		Nb	Mo	40	3
	1000				< 1	5
	1000				< 1	4
	1000		Nb	Mo	31	3
	1015	2400	Nb	Fe	900	13
	1200		Nb	Mo	42	3
	1425		Nb	Mo	66	3
Ta	725	2400	Ta	Fe	19	13
	1000	2400	Ta	Fe	1850	13

TABLE IV (Continued)

Solute	T, °C	Oxygen Content of Li	Source Material	Container Material	Solubility, wppm	Reference
Ti	720				10	17
	730	2400	Ti	Fe	345	13
	800				8	14
	845		Ti		10	17
	900				140	4
	900				140	5
	1000				15	14
	1020	2400	Ti	Fe	3700	13
V	725	2400	V	Fe	150	13
	1010	2400	V	Fe	65	13
W	715	2400	W	Fe	1050	13
Zr	480		Zr		100	15
	700	2400	Zr	Fe	65	13
	760				10000	15
	965	2400	Zr	Fe	250	13
	1000				300	5
	1000				300	4
	1100				1200	4
	1200				3000	5

EXPERIMENTAL METHOD

The basic approach to a solubility study requires that procedures be devised for permitting contact of the solute and solvent at temperature for a given time period, followed by sampling of the equilibrated solution at the test temperature. The entire amount of solvent removed as sample must be analyzed for dissolved solute, since precipitation and segregation take place on cooling.

To meet the requirements of the present program, it was necessary to develop procedures which would not jeopardize the purity of the alkali metal solvents nor permit oxidation or nitriding of the refractory metals and alloys used as solutes. Additionally, each experimental unit had to be completely leak-tight to prevent loss of solvent by vaporization at the high temperatures of this study. An experimental approach which satisfies these requirements was used for an earlier study (20), and much of the same apparatus was employed in the current work. The approach is described briefly below.

To prevent contamination of the high purity materials used, most experimental operations were conducted inside a series of high vacuum chambers. The components for each solubility experiment were assembled, and loaded with potassium or lithium in the high vacuum environment, and were then sealed by electron-beam welding without removing the assembly from the vacuum system. The loaded and sealed crucible-collector assembly was then sealed into an outer capsule of molybdenum (or of T-222 alloy for the 1600°C tests) by electron-beam welding. In tests in which the vapor pressure of the solvent alkali metal was expected to exceed a few tens of torr, a small amount of potassium or lithium was placed inside the capsule to provide a balancing pressure across the crucible-collector wall during the test exposure. The sealed capsule was then heated for the desired time at the test temperature in a furnace in a high vacuum system, while being held in an upright position with the solute crucible at the bottom. At the end of the solubility equilibration time, the capsule was swung out of the furnace at temperature, and cooled rapidly in an inverted position. The solvent metal transfers during the inverting process from the solute crucible to the sample collector, thereby being effectively removed from contact with the solute.

After the solvent had solidified, the outer capsule was opened. The collector was separated from the solute crucible by cutting it with a tubing cutter in a glove box with a purified argon atmosphere. The cut was made far enough from the weld region to preclude the presence of any solid solute metal on the end of the separated collector. The solvent metal was then removed from the collector by melting (for potassium) or dissolution in water (for lithium). The collector wall was treated with an etchant acid to remove the remaining alkali metal from the collector wall, and to dissolve any solute which may have deposited on the metal surface of the collector. All washings were combined into one solution and analyzed for the solute.

Detailed procedures used for the experiments with the two solvents are described below in a later section. Procedures used for the analysis of the solvents for the dissolved solutes are given in Appendix A.

TEST SYSTEM

The environmental test system described in reference (20) was used in the present work. The lithium dispensing equipment described in the section on potassium and lithium handling and transfer, and the new high temperature furnace described below were added for these tests. A number of experiments at temperatures below 1400 °C were completed using the furnace described in the reference report before the new high temperature furnace was in operation. After the new furnace was operable, it was used for all runs.

The new high temperature furnace* has a clam-shell design with the front half hinged to swing forward to allow the test capsule to be swung about a horizontal axis out of the heat zone, and to seat into a water-cooled copper strap quench device. The furnace shell is water-cooled, and packs of tantalum radiation shields are used to reduce the power requirements of the unit. The maximum temperature of the tests reported here was nominally 1600 °C, although the power supply and the materials of construction were selected to permit operation at 1800 °C.

The sample pressure capsule seats into a cup and is supported in place in the furnace hot zone on a T-111 alloy column which in turn is mounted on a T-111 alloy shaft at the bottom of the furnace. Thus, the rotation of this shaft moves the sample capsule from its test position in the furnace hot zone to a position below the furnace at which position the quench device is located. This arrangement is quite similar to that described in reference (20). Figure 1 is a photograph of the furnace in place in Chamber # 4. The furnace was installed in Chamber # 4 by the manufacturer and checked out at the factory under conditions simulating very closely those under which it was expected to be operated in the laboratory. The vacuum chamber containing the furnace was then shipped to this laboratory for final installation in the environmental test system.

Specifications to which the furnace was purchased, and the manufacturer's proof of performance curve of input vs temperature are shown in Appendix B of this report.

The furnace and its vacuum chamber were re-installed in the environmental test system and the manufacturer's representatives demonstrated its performance and conformance to specifications. As a consequence of the demonstration, the decision was made to calibrate each of the W-5Re vs W-26Re thermocouples because their individual variance was greater than was desirable. A jig for calibration in place was made. The calibration results are shown in Fig. 2. The figure shows the thermocouple emf's plotted against the junction temperatures as measured by a calibrated Pt-1%Rh vs Pt-13%Rh thermocouple. Four of the curves agree rather well, and the fifth (#1) lies a little below the group. Thermocouple #2, however, was found to show a large negative discrepancy with the others. Although its readings were rather reproducible in the test, it was found to give unusable results. However, when the other five individual thermocouple calibrations were used for the temperature measurements within the furnace hot zone, the capsule temperature was uniform at the

*Procured from Centorr Associates, Inc., Suncook, New Hampshire.

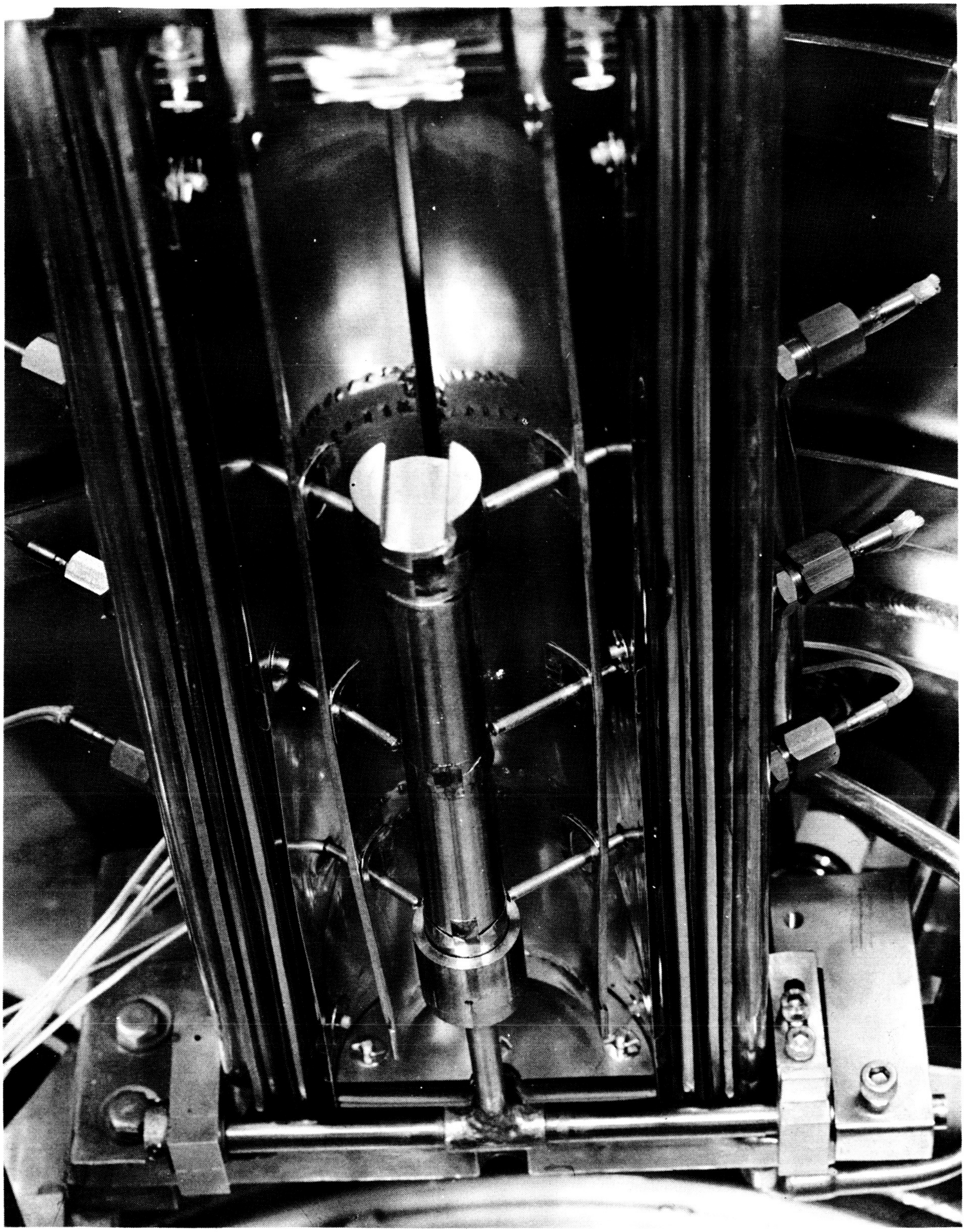


Figure 1. High Temperature Furnace, in Open Position.

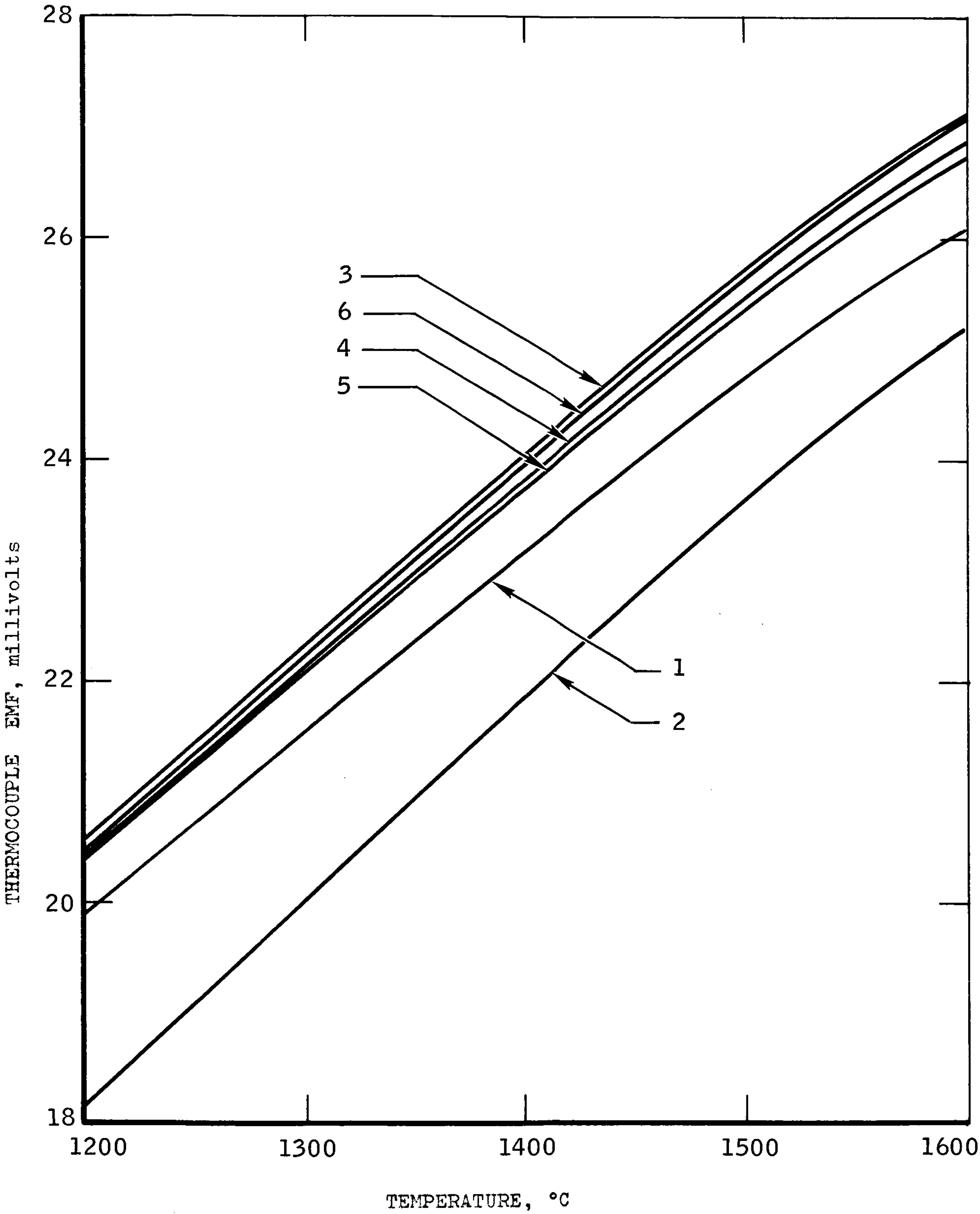


Figure 2. Calibration Curves for W-5Re vs W-26Re Thermocouples.

1400°C level within the normally observed thermocouple temperature measurement uncertainty. The calibration measurements were made in the 1200-1400°C range because of the severe drift of Pt-Rh thermocouples when used above 1400°C. Because of this limitation, it was necessary to extrapolate the calibration curves to 1600°C. This was done as shown in Fig. 2 using the curvature of the manufacturer's standard curve as a guide in the temperature range 1400-1600°C.

The thermocouple temperature measurement was used as described for all experiments with test numbers below 700. However, it was evident that the thermocouples would not be sufficiently durable to accommodate all of the planned series of experiments with lithium solvent. Several of the junctions failed during the potassium experiments, and those which remained proved to be too brittle to permit post-use re-calibration.

Therefore, for the lithium solubility experiments optical pyrometry was used to measure the equilibration temperatures. Mirrors were installed inside the vacuum system at three positions along the length of the furnace such that a solubility capsule in the furnace could be observed through a Micro-optical pyrometer outside the vacuum system. A movable shield was installed to cover the mirrors except when the pyrometer readings were being taken to prevent the deposition on the mirrors of any materials which might be vaporized in the hot zone of the furnace during an experiment. The optical pyrometer was standardized against a standard lamp which had been certified by the National Bureau of Standards*. The window and mirror used for making readings in the high temperature furnace were included in the optical path during standardization. The pyrometer corrections shown in Fig. 3 were applied to all readings.

*Test No. T67298, Atomics International Temperature Standards Laboratory

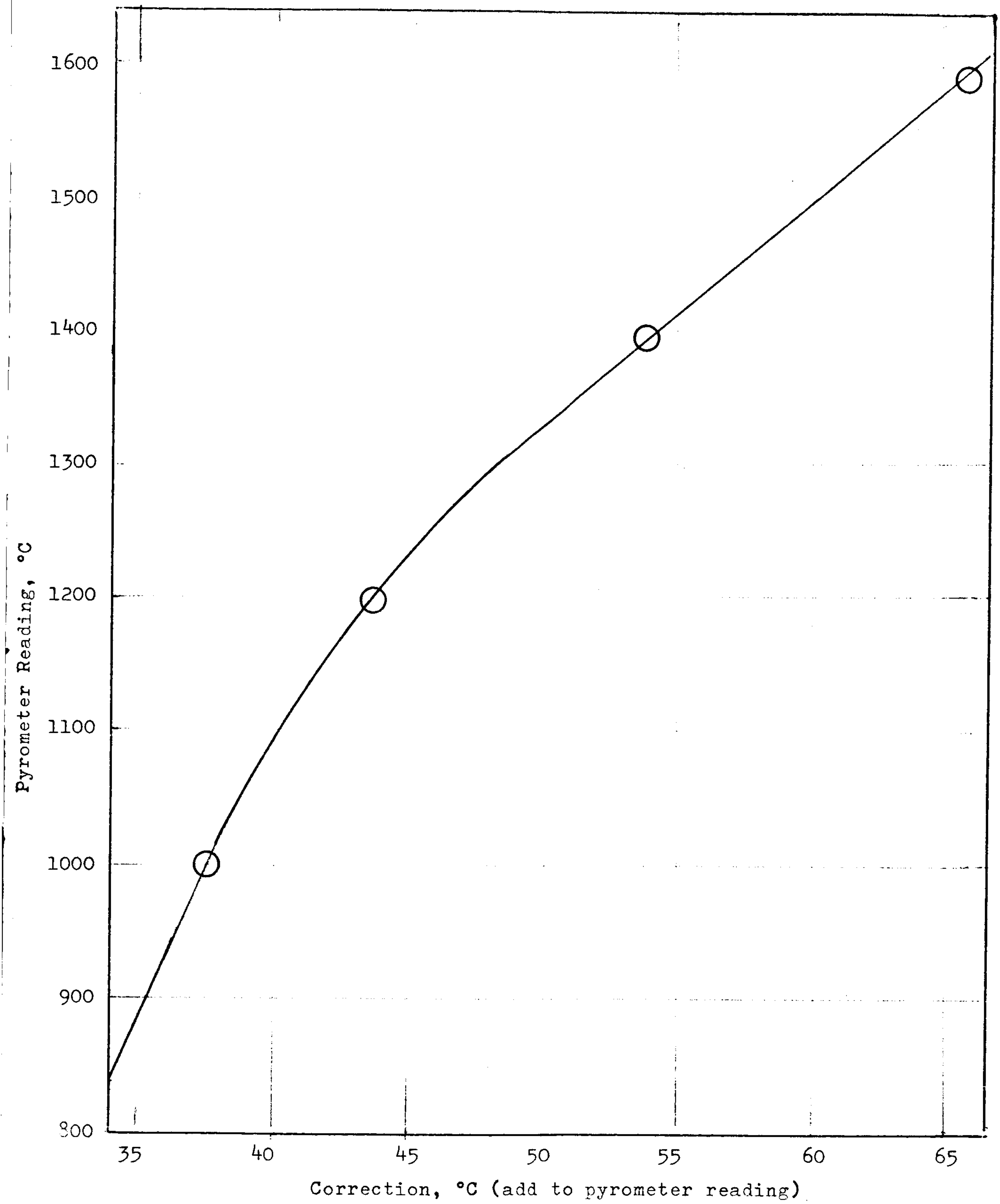


Figure 3. Pyrometer Correction for Reading Through Window and Mirror.

MATERIAL PROCUREMENT

The solute materials used in these experiments can be classified into three main groups, pure metals, advanced commercial refractory alloys, and special alloys. Commercial materials were used for sample collectors and outer capsules. The specifications and/or analyses for these solid metals are given in Appendix C. A general description and source for each material is given in Table V. A description of the potassium and lithium used as solvents is given in a later section of this report.

Solute Materials

Pure Metals - Hafnium, zirconium, and molybdenum were obtained as triple pass electron-beam zone refined rods. The rods were mechanically drilled to make solute crucibles, and chemically treated after drilling to remove machining residues. A crucible fabricated from rhenium sheet was used for rhenium tests, because of the impossibility of obtaining a gettered rhenium alloy within the time and cost limitations of the project. A high purity tungsten crucible was fabricated by project personnel by a vapor deposition process. Tungsten hexafluoride was decomposed to metal in a controlled fashion on the surface of a properly shaped mandrel.

Advanced Commercial Refractory Alloys - The two tantalum-based alloys and one each of niobium (columbium)-based and molybdenum-based alloys were purchased as half-inch rods and machined into solubility crucibles. The alloys T-111 (nominally 8W-2Hf-balance Ta), Haynes Cb-751 (nominally Nb with 1% Zr), and TZM (nominally 0.5 Ti-0.07Zr-balance Mo) were obtained from commercial sources. ASTAR-811C (8W-1Re-1Hf-0.025C-balance Ta) was provided by the program sponsor, NASA-Lewis Research Center.

Special Alloys - It was originally planned to use special alloys of molybdenum, tungsten, tantalum, niobium, and rhenium containing nominally 1/4 to 1/2 percent of zirconium as a gettering addition. The cost of the rhenium alloy proved prohibitive, however. The fabrication of the tungsten alloy into a sound bar from which a crucible could be made was not possible. Therefore the pure metals described above were substituted for the gettered alloys of Re and W. Rods of tantalum, niobium and molybdenum containing about 0.5% Zr were obtained and fabricated into crucibles by machining.

Collector Materials

The Mo-1/2 Ti material used for the collector in all runs, except when analytical chemistry problems prevented its use, was obtained in tubing and rod form. Tubing and rod of Cb-1Zr was obtained for use in experiments in which the solute was Mo, W, or Re.

Capsule Materials

Molybdenum capsules which had been used for the prior program (20) were found to be reusable for the present series of experiments. Sufficient capsule caps remained from the prior work. T-222 alloy (10W-2.5Hf-0.01C-balance Ta) was purchased as fabricated capsule bodies and caps for 1600 °C service.

TABLE V

Compositions and Sources for Solute, Collector, and Capsule Materials

Solutes	Nominal Composition	Source
Hf	100 Hf	Materials Research Corp., Orangeburg, New York
Zr	100 Zr	
Mo	100 Mo	
Re	100 Re	Chase Brass and Copper Co., Rhenium Division, Waterbury, Conn.
W	100 W	Atomics International
T-111	8W-2Hf-balance Ta	J. T. Ryerson and Son, Inc., Chicago, Illinois
Cb-1Zr	Cb-1Zr	Union Carbide Corp., Stellite Division, Kokomo, Indiana
TZM	0.5Ti-0.07Zr-balance Mo	Climax Molybdenum Co., New York
ASTAR-811C	8W-1Re-1Hf-0.025C-balance Ta	NASA Lewis Research Center Cleveland, Ohio
Mo-0.5Zr	Mo-0.5Zr	Westinghouse Electric Co., Astronuclear Laboratories Pittsburgh, Pa.
Nb-0.5Zr	Nb-0.5Zr	
Ta-0.5Zr	Ta-0.5Zr	
Collectors		
Mo-0.5Ti	Mo-0.5Ti	Northwest Industries, Inc., Albany, Oregon
Cb-1Zr	Cb-1Zr	Union Carbide Corp., Stellite Division, Kokomo, Indiana
Capsules		
Mo	100 Mo	Climax Molybdenum Co. of Michigan, Coldwater, Michigan
T-222	10W-2.5Hf-0.01C-balance Ta	Wah Chang Corp., Albany, Oregon

POTASSIUM AND LITHIUM HANDLING AND TRANSFER

The preparation of the ultra pure potassium used in this work is described in detail in reference (20), which includes a discussion of the fractional distillation processes used to obtain the high purity product. All experiments with test numbers between 600 and 644 were carried out with potassium prepared in June 1965, and reported to contain 3.5 ppm of oxygen on the original analysis. The very last potassium remaining in the extruder from which it was delivered into the vacuum system was sampled in January 1967. Analysis of duplicate samples for oxygen gave results of 6 and 7 ppm, or an average of 6.5. Within analytical chemical uncertainty for analyses at this oxygen level, this number is not significantly different from the analysis of the first potassium used from the extruder. From this it was concluded that the integrity of the potassium was not degraded by long storage in the extruder, and that the concept of using an extruder as a purified potassium distillate collector-storage vessel-dispenser unit is a sound one.

After the last portion of the previous batch of potassium had been sampled, a new batch was prepared. The purification unit was cleaned by running a batch of potassium through the complete purification procedure to rinse all the internal surfaces of the apparatus with freshly distilled pure potassium. This product was then discarded and a second still loading put through the process to produce a new batch of purified potassium. Oxygen analysis of the potassium in the newly filled extruder showed 5 ppm, indicating that the potassium used in all experiments had substantially the same impurity content. Analysis of the distilled potassium is shown in Table VI. All potassium solubility experiments with test numbers below 600 or above 644 were carried out with the batch of potassium purified in January 1967.

The potassium handling and transfer operations were carried out as described in an earlier report (20). In brief, the approach used is one which does not jeopardize the potassium purity after the purification process. To this end, the purified potassium was extruded directly into a high vacuum system. The extruded material was cut with a wire "cheese cutter", which was then heated by passing an electric current through it in order to release the potassium from the wire by melting. The potassium sees no environment other than this high vacuum, since the final capsule closure weld is made without removing the parts from the vacuum system.

Four preliminary solubility experiments were carried out with hot trapped lithium as the solvent. The lithium was hot trapped with a zirconium foil getter for 126 hours at 820°C by the supplier*, who also supplied the analysis given in Table VII.

All other lithium solubility experiments used highly purified lithium solvent obtained from the same source. This lithium was prepared by distillation. Table VII shows the impurity levels as reported by the supplier. The analysis for oxygen in lithium is not straightforward, but the 33 ppm number reported reflects the average of nine analyses from two laboratories. Without a doubt the lithium which was used is the highest purity material available for solubility experiments, and is of very high quality.

*General Electric Corp., Missile and Space Division, Cincinnati, Ohio

TABLE VI

Analysis of Distilled Potassium Solvent

Element	Analysis wppm	Element	Analysis wppm
Ag	< 1 ND*	Mg	< 1 D
Al	< 1 D*	Mn	< 1 ND
B	<10 ND	Mo	< 1 ND
Ba	<10 ND	Na	5 D
Be	< 1 ND	Ni	< 5 ND
Bi	< 1 ND	O	5 D
Ca	< 5 D	Si	< 5 ND
Cd	< 1 ND	Sn	< 5 ND
Co	< 5 ND	Ti	< 5 ND
Cr	< 1 ND	V	< 1 ND
Cu	< 1 ND	Ta	< 2 ND
Fe	< 1 ND	Zr	<10 ND
Li	< 1 ND		

*ND = not detected, D = detected at the level shown

TABLE VII

Analyses of Lithium Solvents

Element	Analysis, wppm* Hot-trapped Li	Analysis, wppm* Distilled Li	Element	Analysis, wppm* Hot-trapped Li	Analysis, wppm* Distilled Li
Ag	< 5	< 5	Mo	< 5	< 5
Al	5	< 5	N	15	13
B	<50	<50	Na	80	<25
Ba	--	<50	Nb	--	<25
Be	5	< 5	Ni	28	< 5
C	73	44	O	115±15	33
Ca	5	< 5	Pb	<25	<25
Co	< 5	< 5	Si	28	< 5
Cr	< 5	< 5	Sn	<25	<25
Cu	28	< 5	Sr	--	< 5
Fe	5	< 5	Ti	< 5	<25
Mg	< 5	< 5	V	< 5	<25
Mn	< 5	< 5	Zr	< 5	<25

* With the exception of C, O, and N, all results are from emission spectrography. The numbers shown represent the minimum concentration of impurity that could have been detected by the method as applied.

The lithium was shipped in a stainless steel cylinder which was fitted at both ends with bellows-sealed stainless steel valves. The shipping container was connected to a small calibrated volume, which in turn was fitted to a flange to replace the lighting window on the top of Chamber # 1, as shown in Fig. 4. Heaters to melt the lithium for transfer, and a purified helium gas supply were installed.

The loading with lithium of a crucible-collector assembly was accomplished before it had cooled completely, following the desorption heating in the furnace in Chamber # 1. While the furnace temperature was still above the melting point of lithium, the crucible-collector assembly was removed and held in the jaws of the manipulator so that the end of the beveled delivery tube from the lithium supply was about 1/4 inch inside the top of the collector. Then the calibrated volume was filled with lithium by opening the valve between it and the large cylinder, and applying about 3 psia of helium pressure to the top of the cylinder. This valve was then closed, and the same helium pressure applied to the calibrated volume. The helium valve was closed again, so that when the final delivery valve was opened there would not be a direct connection from the helium supply to the vacuum system. The bubble of helium which remained in the calibrated volume from this procedure was sufficient to push the lithium out through the delivery valve into the crucible-collector assembly, when the valve was finally opened. The operation was monitored visually, since it was possible to see the lithium pass the beveled end of the delivery tube. After the lithium had transferred, the calibrated volume was open to the vacuum chamber, so when the delivery valve was closed the apparatus was immediately ready for another loading sequence. The filled assembly was held in Chamber # 1 until the lithium solidified, and was then passed into Chamber # 2 for welding.

Early in the experience of handling liquid lithium, it was found that the low density and high surface tension of the material made it difficult to transfer by gravity methods. Specifically, it was found to be impossible to transfer the solvent lithium from the solute crucible into the sample collector by inverting the assembly at temperature following completion of a solubility test, although this procedure is always effective with potassium and sodium. A comparison of the surface tension/density ratios for a number of liquid metals is shown in Table VIII. It is not surprising, in light of the ratios in the table, that the simple gravity method of transfer fails with lithium.

TABLE VIII

Surface Tension-to-Density Ratios for Liquid Metals

Metal	Surface Tension/Density, dynes/cm/gm/cu cm	Temp. °C
Li	720	550
Mg	360	680
Hg	320	300
Al	220	750
Na	210	550
K	120	550
Pb	40	550

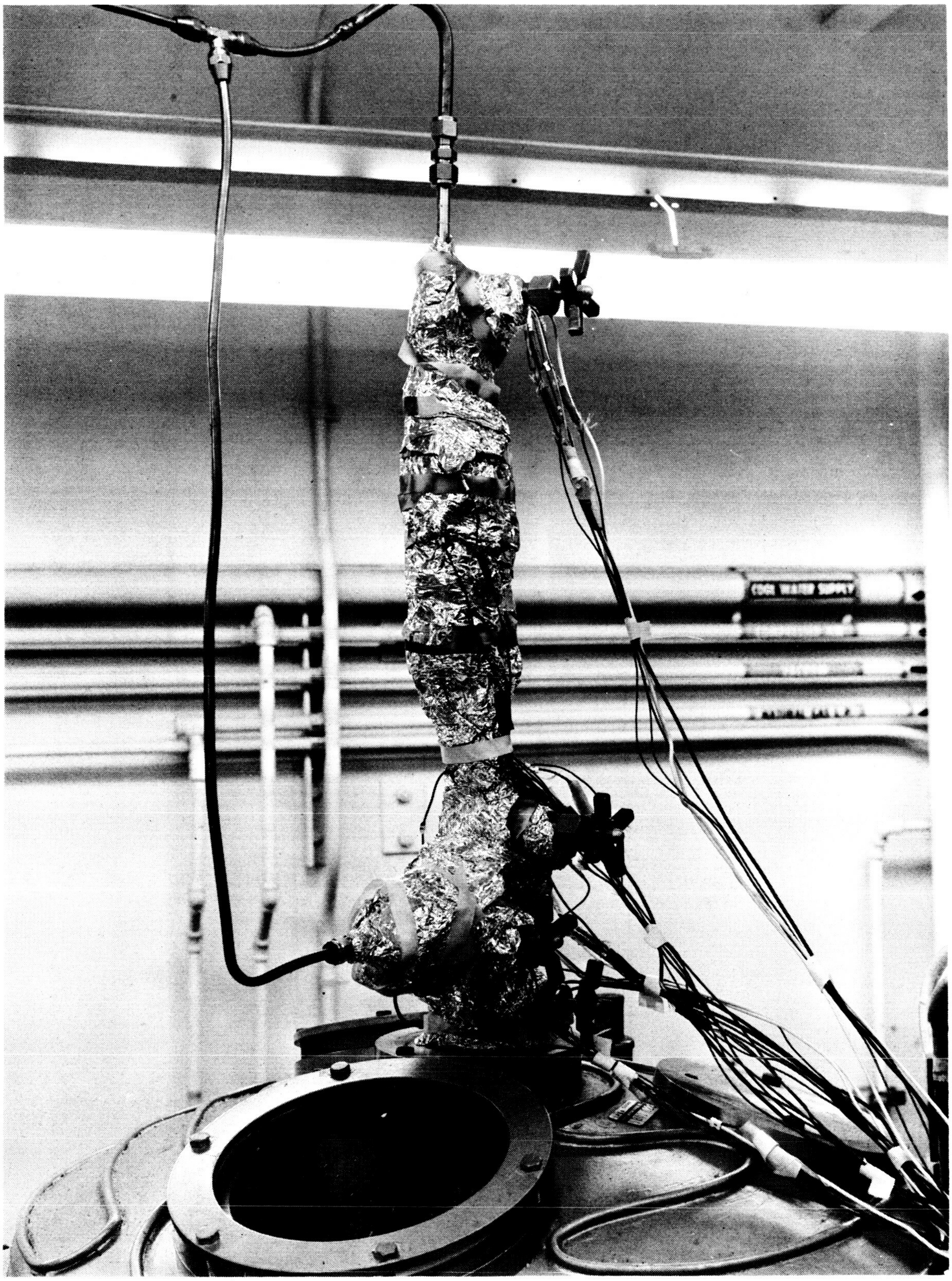


Figure 4. Lithium Storage and Dispensing Apparatus.

Three methods of effecting the transfer of lithium from the crucible to the collector were investigated. In one of these, the solenoid rapper method, the experimental capsule was externally agitated in an effort to break the surface of the lithium, permitting it to flow. In the other two methods the surface of the lithium was broken by using additional parts within the crucible-collector assembly. These latter two methods therefore have the potential disadvantage of introducing an additional material into the solubility experiment, but this was considered a small price to pay to insure that the lithium would transfer properly. Details of these three methods are as follows:

Solenoid Rapper - A sealed solenoid coil is used to drive an armature repeatedly against the side of the capsule, transmitting the vibration to the collector inside the capsule. The solenoid is activated externally for a given length of time.

Internal Heavy Metal Ball - In this approach, a ball of an inert metal, e.g., W or Re, is added to the crucible during the loading operation. When the assembly is inverted at temperature at the end of a solubility test exposure, the sphere is above the lithium which adheres to the crucible, and falls through it like a loose-fitting piston. In theory, this breaks the meniscus, initiating the flow of the lithium into the collector.

Internal Wire - A wire of inert metal, e.g., W or Re, placed on the inside of the crucible-collector assembly, and positioned so as to be nearly touching the wall, provides a capillary path for the lithium to flow along. During the test exposure, the lithium may crawl upward along the wire, but this should not interfere with the attainment of equilibrium between the solute and solvent. When the test is complete and the capsule is inverted, the wire provides a path down which the lithium can flow, because the effective diameter of the lithium column adjacent to the wire will be much smaller than that of the crucible, and, in addition, the head of lithium will tend to drive the metal down along the wire. The capillary rise (in a cylindrical column) is given by, $h = \sigma/r\rho g$, where σ is the surface tension, dynes/cm; r is the radius of the column, cm; ρ is the field density, gm wt/cu cm; g is the gravitational constant, 980.7 dynes/gm wt, and h is the column height in cm. Therefore, as r is reduced h increases, so that there is more tendency for the lithium to move along the wire (where the effective r is small) than to remain bridged across the larger crucible diameter.

Table IX shows the results of tests of these three methods for facilitating the transfer of lithium from the crucible to the collector.

On the basis of these tests, the internal wire method was chosen for routine use in the lithium solubility experiments. It proved to be reliable and effective, failing to operate successfully only in one case, in which the transfer wire had failed to remain close to the wall of the collector.

TABLE IX

Lithium Transfer Tests

Transfer Aid	Temp. °C	% Transfer
Solenoid rapper, 1 minute	1350	34
Solenoid rapper, 1/2 minute	1185	0
Solenoid rapper, 2 minutes	1040	16
Tungsten sphere	1040	90*
Tungsten sphere	1110	> 98
Tungsten wire	1120	> 98

*Only 0.25 gm of Li was loaded, with less than 0.025 gm not transferred. This latter amount remained behind in the tests in which > 98% transferred.

SOLUBILITY TEST PROCEDURE

Solubility Experiment Components

The components used for each solubility experiment are solute crucible, collector, collector cap, capsule, capsule cap, and in lithium experiments, a transfer wire. Figure 5 is a cross-sectional representation of the assembled components for a solubility experiment. The numbers indicate the sequence of operations for loading and welding the components. Typical crucible-collector assemblies, before being loaded with solvent metal, are pictured in Fig. 6. A welded pressure capsule, after completion of the loading sequence, is shown in Fig. 7. Details of the operations are given below.

Outgassing of Components

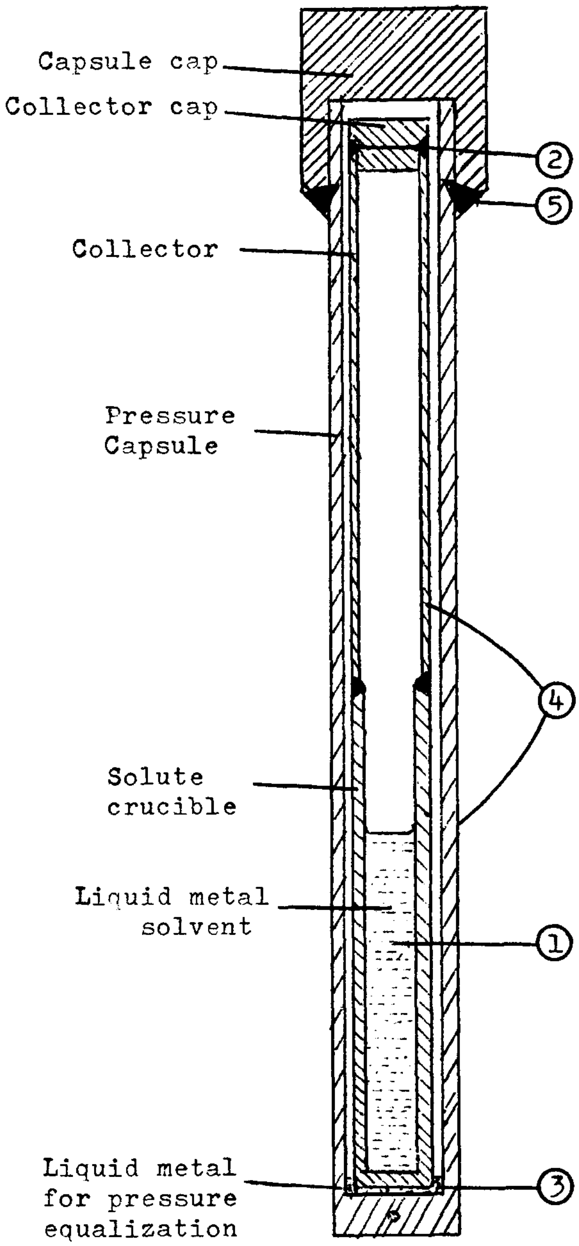
Solute crucibles were chemically etched after machining to remove surface contamination. After rinsing and drying, the crucibles were vacuum outgassed at a temperature about 100 °C in excess of their maximum solubility test temperature, and were held at this temperature until the pressure in the vacuum system dropped back to 2 x 10^{-6} torr, which was the pressure in the system before heating. After the outgassing furnace had cooled under vacuum, it was filled with an atmosphere of argon in all cases.

The collectors and caps were degreased and then etched in a mixed acid solution consisting of 50 HNO_3-30 H_2SO_4-20 H_2O plus one drop of HF per 5 ml of mixed acid. This mixture gives a controllable, but reasonably rapid, etch and removes tool marks and surface contamination. After rinsing and drying with acetone, the collectors were outgassed at 1600-1650 °C under vacuum until the pressure dropped to 2 x 10^{-6} torr.

The molybdenum outer capsules and caps were degreased in acetone and then outgassed under vacuum at 1800-1900 °C until the pressure had dropped to 2 x 10^{-6} torr. The T-222 alloy pressure capsules and caps were similarly degreased and then outgassed at 1650-1700 °C until the pressure had dropped to 2 x 10^{-6} torr. This treatment is more severe than the annealing treatment usually quoted for T-222 - 1320 °C for one hour - but since this testing program called for heating at 1600 °C for four hours it was necessary to pre-treat the components at the higher temperature to ensure that there would be no appreciable outgassing during the solubility test.

All test components were subjected to a further heating at 350 °C in the desorption heater in vacuum chamber #1 immediately prior to loading. This heating removed any argon or other gas which may have been adsorbed on the surface during the transfer of the parts subsequent to the high temperature outgassing.

The time between the high temperature outgassing of alloy solute crucibles and the solubility test itself was minimized for the last half of the solubility runs, in order to reduce the possibility that metallurgical changes during this period could affect the solubility experiments. The time period did not exceed 72 hours for those experiments in which it was controlled.



Sequence of Capsule Loading Operations
(all carried out in high vacuum)

1. Load crucible-collector assembly with liquid metal solvent.
2. Weld cap on crucible-collector assembly.
3. Place liquid metal for pressure equalization in pressure capsule.
4. Place welded crucible-collector assembly in pressure capsule.
5. Weld cap on capsule.

Figure 5. Solubility Experiment Components (Cross-Section View), Full Size, Showing Sequence of Loading Operations.

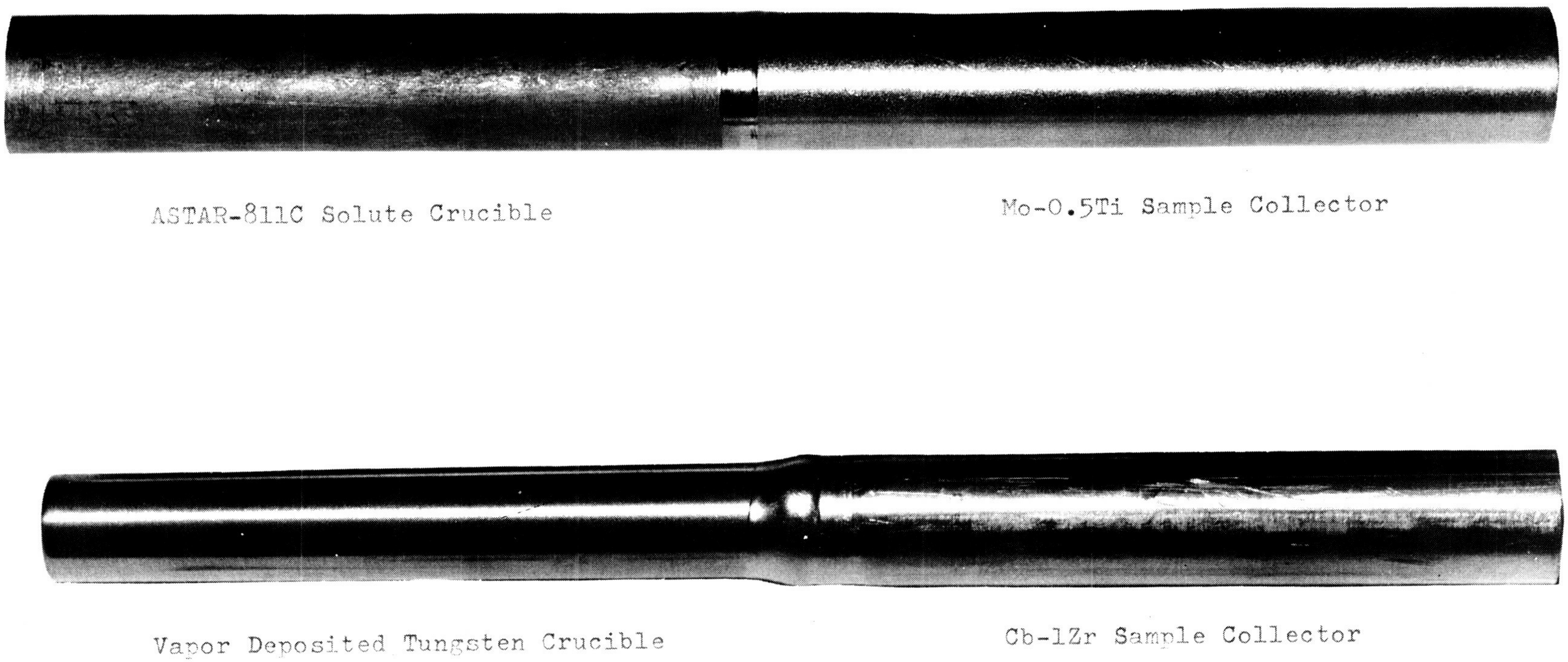


Figure 6. Welded Crucible-Collector Assemblies, One and One-Half Times Actual Size.

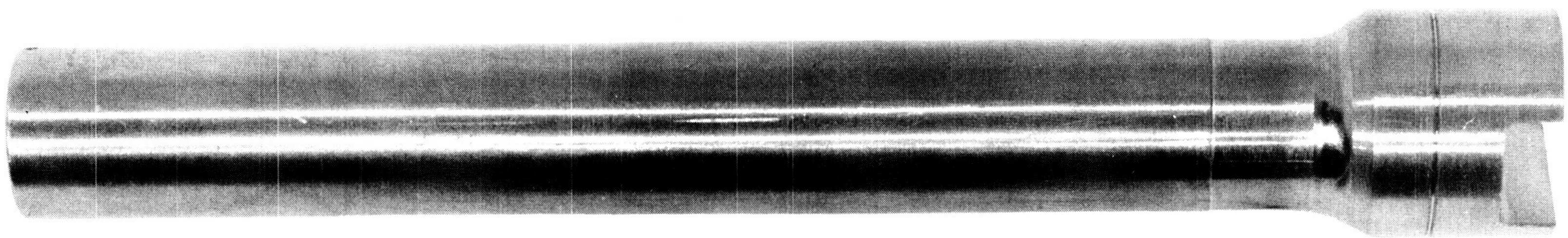


Figure 7. Welded Pressure Capsule (T-222 Alloy), One and One-Quarter Times Actual Size.

Crucible-Collector Welding

Outgassed solute crucibles and collectors were electron-beam welded under high vacuum to produce assemblies like those shown in Fig. 6. If the difference between the melting points of the two parts is large, this weld is more properly termed a braze, in which the lower melting point metal is fused and flows onto the higher melting point metal. For example, the joint between a zirconium solute crucible (m.p. 1830 °C) and a Mo-1/2 Ti sample collector (m.p. 2600 °C) is really formed by melting the zirconium, which wets the molybdenum alloy and makes a metallic bond with it, perhaps with small amounts of intermediate solid solution and intermetallic compound phases.

The crucible-to-collector welding operation provides a possible source of error in solubility experiments, because of the possibility that crucible material may vaporize in the weld zone and deposit in the sample collector. The weld lip of the solute crucible was generally on the inside of the sample collector lip, and line-of-sight evaporation could have caused deposition of solute on the inside of the collector. For example, in the case of a T-111 solute crucible and a Mo-1/2 Ti collector, the Mo alloy was melted by the welding beam and dissolved some of the T-111 to make the seal, but the bulk of the T-111 did not melt, although it became quite hot under the molten Mo alloy. The inner lip of T-111 ensured that the molten Mo alloy could not flow down inside the crucible. The melting point of Mo is 2890 °K, and that of the alloy should be somewhat lower. The estimated temperature of the molten weld material is therefore taken to be 2900-2950 °K, and the temperature of the inner wall of the T-111 can be reasonably taken to be, say, 2850 °K in the vicinity of the weld spot. Thus, this spot can be considered to be a Langmuir evaporation source for tantalum, and the evaporation can deposit tantalum on the inside of the collector and the crucible, also.

For a temperature of 2850 °K, Stull and Sinke (24) give the vapor pressure of Ta as about 10^{-7} atm, and the Langmuir equation for the evaporation of Ta(g) predicts an evaporation rate of 1.2×10^{-6} gm/sec sq. cm. For a spot 0.5 cm x 0.5 cm = 0.25 sq cm, and a total weld period of 10 seconds, the amount of tantalum which would evaporate from a pure Ta surface would be 1.2 x 0.25 x 10 = 3 micrograms Ta. Since T-111 is 90% Ta, the loss of Ta from T-111 should also be about 3 micrograms under these conditions. This 3 μgm value is quite sensitive to the time, area, and temperature assumptions used. For example, if the temperature were 2950 °K and the time were 20 seconds, the v.p. increases by a factor of 3, and the time by a factor of 2, so that the predicted Ta transfer becomes 18 μgm. To provide experimental verification for this hypothesis, experiments were carried out in which a tungsten rod was inserted into the sample collector during the welding process, and subsequently chemically etched and the solution analyzed for tantalum. It was found that appreciable amounts of Ta - from a few micrograms to several tens of micrograms - could be recovered from the tungsten shield. Therefore the routine procedure after these experiments included a skin-cut machining operation on the inside of the collector following the crucible-to-collector weld. This machining was easily performed through the open end of the collector, since the cap had not yet been welded on (see Fig. 5). Specific problems in the joining of some crucible materials to their collectors are discussed in the "Results and Discussion" section of this report.

Loading of Potassium

The potassium loading procedure was essentially the same as that described in Reference 20. After removal from the desorption heater, the crucible-collector assembly was placed upright in a fixture on the floor of the vacuum chamber. The loading funnel, which had been heated well above the melting point of potassium, was placed in the collector. Then about two grams of potassium was extruded, cut off with the hot-wire cutter, and dropped into the funnel, through which it ran into the crucible-collector assembly. The funnel was then removed and the potassium permitted to solidify. A small amount of potassium (about 1/4 gram) was placed in the outer capsule by a similar procedure, to equalize the pressure inside and outside the crucible-collector assembly. Because of the larger diameter of the capsule the heated funnel was not needed for this latter operation.

All parts (loaded crucible-collector, capsule with small amount of potassium, and caps for both) were then passed through the high vacuum gate valve into chamber #2, the welding chamber, in which the cap was welded onto the collector, and the sealed crucible-collector assembly was placed in the pressure capsule. Then the capsule cap was welded in place. The sealed capsule was then ready for the solubility equilibration at temperature.

Loading of Lithium

The loading of a crucible-collector assembly with lithium differed from the procedure for potassium in that the lithium was transferred as liquid from the supply cylinder to the solubility assembly, as described in a prior section. In addition no lithium was added to the pressure capsule body (outside the crucible-collector assembly) because the vapor pressure of lithium is not so great at the test temperatures that this measure is necessary to prevent the swelling of the crucible-collector assembly. After the lithium is loaded into the crucible, and has solidified, the closure welds are completed in the same manner as for the potassium experiments.

Equilibrating at Temperature

The welded solubility capsule was installed in the high temperature furnace in an upright position, as seen in Fig. 1, and the movable half of the furnace swung into place. Power to the furnace was turned on when the pressure in the vacuum system was reduced to the low 10^{-6} torr range. Timing was begun when the capsule reached the desired equilibration temperature. At the end of the equilibration time, the power was turned off, the furnace opened, and the capsule inverted by rotating it out of the furnace into the chill trap, all in rapid sequence. When the furnace had cooled sufficiently, the vacuum system was filled with argon and the capsule removed for opening.

Preparing for Analytical Chemistry

The first step in preparing solubility runs for chemical analysis was to cut open the outer capsule in order to remove the crucible-collector assembly. This was done by machining away the capsule closure weld. For experiments using potassium solvent, the inner assembly was then carefully washed with water to remove potassium that adhered to the outside of it. The entire crucible-collector assembly, still sealed, was then given to the analytical chemist. For experiments using lithium solvent, the collector was cut off with a tubing cutter, in a purified argon glove box, with the cut made sufficiently far from the weld area to preclude the presence of any of the crucible material in the cut-off portion. The collector, containing the lithium, was then heated on a hot plate in the glove box until the lithium melted and the sample transfer wire could be removed. After the wire was removed, the lithium was allowed to solidify. The collector was then placed in a conical flask which was closed with a rubber stopper, and given to the analytical chemist. Analytical methods employed are described in Appendix A.

It has been suggested that the apparent solubilities measured might be low because solute atoms could diffuse along grain boundaries in the collector to such as extent that the routine etching procedure used in the analytical chemistry would not remove it all. (This diffusion period is effectively limited to the time during which the sample is being quenched.) To test this hypothesis, lathe cuts of about 0.001" were taken on the internal surface of two Mo-0.5 Ti collectors which had been used in tantalum experiments, and one unused collector. This was repeated to collect nine samples of turnings, three sequential cuts on each of the three collectors. In addition, a solid piece of unused collector was analyzed. These ten samples were analyzed using a spark source mass spectrometer. The results are shown in Table X.

The intensity of the tungsten line was used as an internal standard in the analysis. The presence of appreciable amounts of Nb, Zr, and Hf in sample C-2 indicates contamination after the machining operation, and the high tantalum number must therefore be attributed to contamination. A comparison of the other results indicates no evidence that tantalum has penetrated into the collector surface. The amount of tantalum found in the cuts from the two collectors (#37 and #38) are no higher than that in the solid molybdenum piece or the first and third cuts from the unused collector (C-1 and C-3). It therefore seems very unlikely that reported solubilities might be low because of loss of tantalum into the collector material.

TABLE X

Spark Source Mass Spectrometer Analysis of Samples from the Interior Surfaces of Mo-0.5Ti Sample Collectors

Sample	Parts per million (weight)				
	Ta	W	Nb	Zr	Hf
Solid Moly Piece	2.3 - 7.7	80	n.d.*	n.d.	n.d.
38-1	2.8 - 6.2	80	n.d.	n.d.	n.d.
38-2	3.6	80	n.d.	n.d.	n.d.
38-3	0.62	80	n.d.	n.d.	n.d.
37-1**	~ 1	80	~ 1	~ 1	n.d.
37-2	2.6 - 4.3	80	~ 300	n.d.	n.d.
37-3	0.6 - 0.9	80	n.d.	n.d.	n.d.
C-1	4.7 - 16	80	n.d.	n.d.	n.d.
C-2***	58 - 170	80	~ 1%	~ 300	13 - 28
C-3	2.5 - 3.8	80	n.d.	n.d.	n.d.

* **n.d.** = not detected in ppm amounts

** The W/Mo ratio in this sample was significantly larger than was observed in the others. However, the ratio of tungsten to the listed metals is essentially the same as was observed for the other samples.

***The amounts of Nb, Zr, and Hf in this sample indicates gross contamination in some step of the machining and handling process.

ANALYTICAL PROCEDURE DEVELOPMENT STUDIES

As solubility experiments progressed, it became apparent from the scatter of the data and the poor analytical reproducibility for tantalum, that some refinement of the analytical method for this element was required.

The spectrophotometric method originally reported by Luke (18) utilized the color developed by tantalum with phenylfluorone (2,3,7 - trihydroxy - 9 phenyl - isoxanthene - 3 - one) which exhibits an absorption maximum at 530 nm. Luke's method involves the following steps:

1. Evaporate an aliquot portion of the sample solution to dryness in a water bath.

2. Take up in an acid mixture and extract with methylisobutylketone.

3. Evaporate methylisobutylketone extract to dryness.

4. Fume with HNO_3 and $HClO_4$.

5. Add reagents for development of colored tantalum-phenylfluorone complex, and read after 30 minutes at 530 nm on a spectrophotometer.

Luke studied the method using 0, 40, 80 and 120 μg of Ta. The presence of Mo interferes because the Mo-phenylfluorone complex reportedly exhibits an absorption maximum at 565 nm. The addition of EDTA prior to color development to complex up to 1 mg of Mo eliminates the Mo interference, according to Luke. Additional Mo must be removed by a hexone extraction of the Ta-F complex.

This method was verified at AI over the range 0-50 μg Ta in samples containing up to 50 mg Mo. Hill (9) reported Luke's method to be unreliable for less than 40 μg of Ta due to Ta loss during Luke's evaporation steps, and he developed a modified analytical scheme which avoided the strong evaporation step. Hill's modifications to Luke's method permitted determination of 2-50 μg Ta to about ± 5% (relative) at 10 μg.

Attempts to verify Hill's data have provided an interesting and revealing series of observations. In agreement with Hill, it was found in the present study that at least one hour is necessary for optimum color development as opposed to 30 minutes as reported by Luke. Precise and exact replication of the quantities of reagents (and in the specified order) is required to obtain a meaningful and reproducible blank. The previous difficulty can probably be attributed to slight variations in reagent quantities which could affect the overall equilibrium of the system. Phenylfluorone exhibits an extremely strong absorption band at 490 nm and the shoulder of this band exerts an influence at 530 nm. The absorption spectrum was not described or discussed by Luke or Hill. If this contribution of the "shoulder" at 530 nm is not a constant influence, then poor analytical reliability must result. Improved reliability might be gained at the expense of sensitivity by reading at 560 nm, if the Mo extraction is complete(and/or if EDTA complexes any remaining Mo).

Hill's publication (9) provided the basis for the work described below to determine the precision of measurements in the 0-10 microgram tantalum range, and to discern the extent, if any, of interferences caused by the presence of molybdenum or lithium.

To this end a series of "standard curves" was prepared as follows: (1) tantalum only, (2) tantalum plus molybdenum, (3) tantalum plus lithium, and (4) tantalum plus molybdenum plus lithium. In each case the solutions were carried completely through the phenylfluorone method. The data were treated by analysis of variance techniques which look at the regression lines drawn through each set of data and the single line drawn through the pooled points. By determining the sum of squares of deviations from the best line through all the data, from the best line through the individual sets with a pooled estimate of the slope, and from the best line through the individual sets each with its own slope, one can examine the ratios of these sums of squares at the appropriate degrees of freedom and apply an F test to determine any significance. A statistical analysis of the results of these experiments is given in Appendix D.

The experimental data demonstrate that in the 0-10 μg Ta range essentially complete recovery is effected using extraction methods, and in cases where Mo collectors and Li solvents are involved, standard curves prepared from impurities of the same order of concentration as the samples can be expected to yield a ± 1 μg uncertainty (95% confidence level). This uncertainty is that expected for aqueous solutions of tantalum in this concentration range. When the uncertainties associated with the rest of the solubility measuring technique (e.g., thermal equilibration, solvent transfer, collector cutting, and alkali metal dissolution) are included, the uncertainty for a specific measurement of tantalum concentration is about ± 3 ppm.

RESULTS

In this section, the results of the solubility experiments are discussed by individual solute-solvent combinations, with the potassium work first, followed by the lithium work.

T-111 in Potassium

The results of experiments with T-111 alloy solute crucibles, and Mo-1/2 Ti sample collectors, with potassium solvent, are shown in Table XI. These points are plotted in Fig. 8, with the exception of runs #607 and #612, which are considered unreliable. The crosses (+) represent experiments carried out in the first series, before the development of the improved analytical method for tantalum and before the sample collector's internal surface was routinely machined after welding. The two points denoted (X) are experiments in which a tungsten shield prevented the deposition of tantalum on the surface of the sample collector during welding, but the analysis for tantalum in the potassium was carried out by the unimproved method. The four points denoted by open circles are from experiments in which tantalum deposited during welding was mechanically removed from the collector surface before loading with potassium, and the improved tantalum analytical method was used. The curve shown is described by the equation $\log_{10} S(\text{wppm Ta in K}) = 2.099 - 2090/T(°K)$, the slope of which yields a heat of solution of about 9600 calories per mole. If a curve were drawn through the crosses (+), excluding # 637, its slope would be very nearly the same as that for the curve shown.

In an attempt to determine whether or not the presence of a pure getter surface in the vapor space above the potassium would have any effect on the apparent solubility of tantalum from the alloy, an experiment was run in which there was a hafnium section inserted between the T-111 solute crucible and the Mo-1/2 Ti collector. The welded assembly is shown in Fig. 9. The hafnium section was about 3/4 inch long, and was salvaged from the hafnium crucible used in tests #609, #621, and #641. Problems encountered with the hafnium crucible in these tests are discussed below. In using the hafnium in the test with T-111 solute, some difficulty was experienced in making the composite crucible-collector subassembly, but it proved to be helium leak tight at the time the potassium was loaded. However, after the test it was found that a leak had developed in the hafnium wall and a large fraction of the potassium had escaped from inside the crucible. Therefore, the sample was not analyzed.

ASTAR-811C in Potassium

The results of three experiments with ASTAR-811C solute crucibles and Mo-1/2 Ti sample collectors, with potassium solvent, are shown in Table XII. The tantalum analyses used the unimproved analytical technique, and the tests were run before the measures to prevent vapor deposition of solute during the welding process were instituted. Therefore the conclusion that can be drawn from the data is that the solubility of tantalum from the alloy is in the 6 to 10 wppm range over the temperatures of these experiments, with no definable temperature dependence from these data.

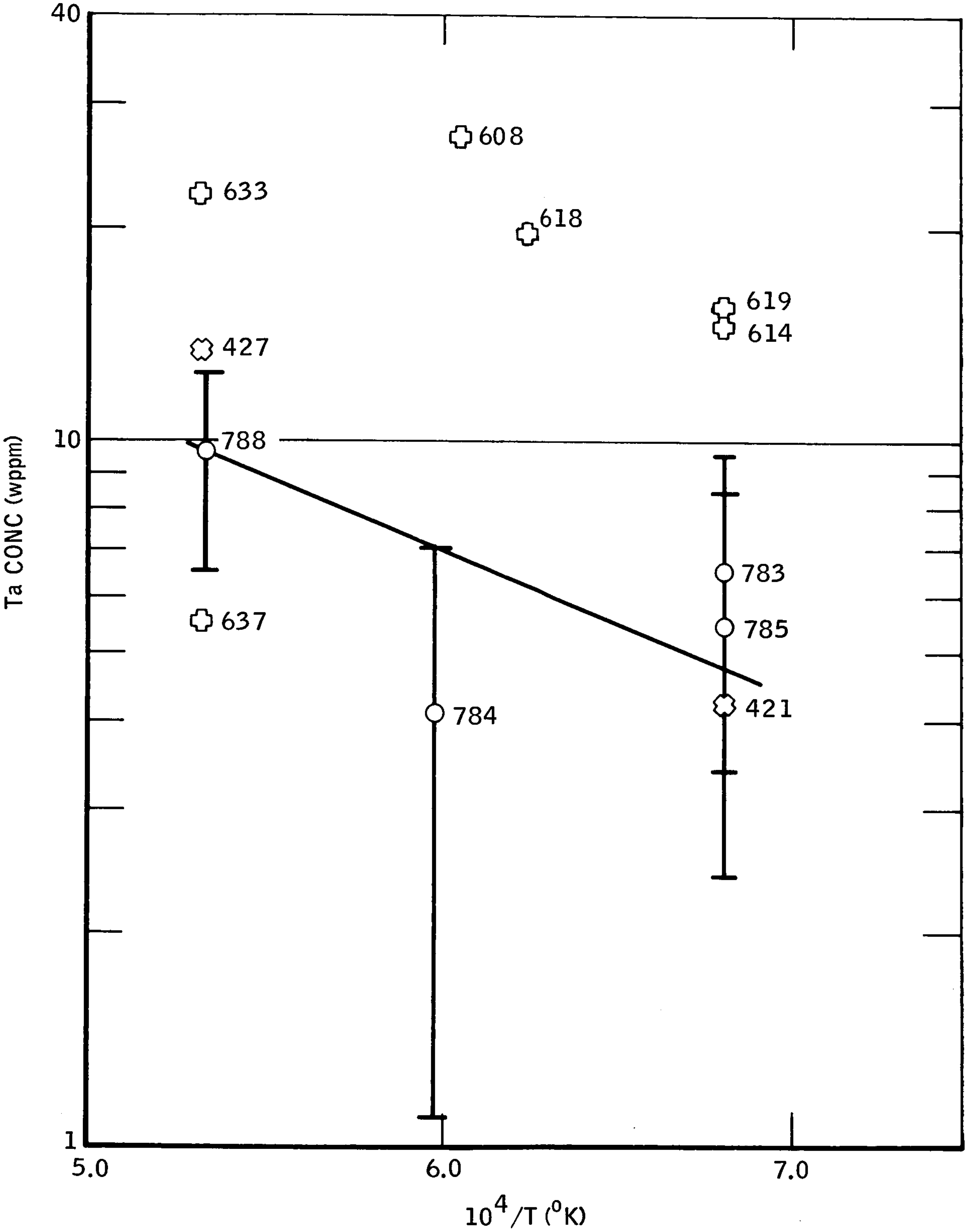
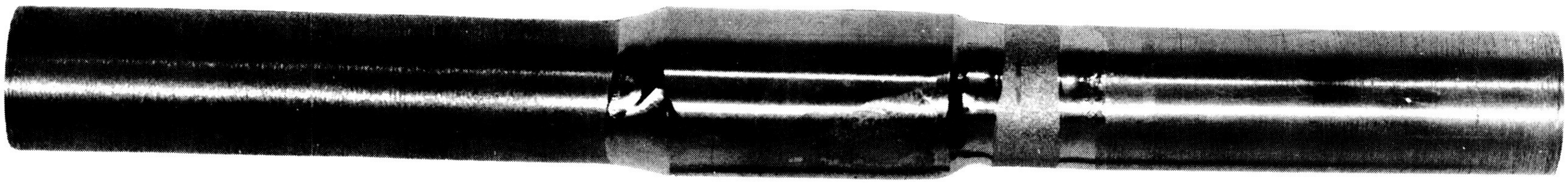


Figure 8. Solubility of Tantalum from T-111 Alloy in Potassium.



T-111 Solute Crucible

Hafnium Getter Section

Mo-0.5 Ti Sample Collector

Figure 9. Crucible-Collector Assembly with Hafnium Getter Section, One and One-Half Times Actual Size.

TABLE XI

Concentration of Tantalum from T-111 Alloy* in Potassium

Test No.	Temp., °C	Time, hr.	K, gm	Ta, μg	Ta, wppm
421	1200	4	1.62	7	4.3
612	1200	4	1.37	46	39.0
614	1200	4	1.58	23	14.7
619	1200	4	2.1	33	15.5
783	1200	4	1.4	9	6.5
785	1200	4	1.2	6.5	5.4
618	1329	4	1.85	37	19.8
607	1382	4	1.87	< 0	Negative Result
608	1382	4	2.0	47	24
784	1400	4	2.0	8.2	4.1
788	1600	4	1.65	15.8	9.6
637	1608	4	1.60	9	5.6
633	1613	4	1.70	38	22.3
427	1615	4	1.68	23	13.7
789	Control at 12 μgm Ta			13.0	

* Nominal compositions for all solutes are given in Table V.

TABLE XII

Concentration of Tantalum from ASTAR-811C Alloy in Potassium

Test No.	Temp, °C	Time, hrs.	K, gm.	Ta, μgm	Ta, wppm
636	1261	4	1.70	12.5	7.4
638	1405	4	1.75	16	9.2
642	1625	4	2.03	12	6

Tantalum-0.5% Zirconium in Potassium

The results of eight experiments with a nominal Ta-1/2% Zr alloy and Mo-1/2 Ti sample collectors, with potassium solvent, are shown in Table XIII. The tantalum analyses used the unimproved analytical technique, and the tests were run before the measures to prevent vapor deposition of solute during the welding process were instituted. The very wide spread of the data is confusing. Some of these samples were analyzed concurrently with some of those from T-111 and ASTAR-811C runs in which only a few micrograms of Ta were found. Two different crucibles were used, but both of them showed the same wide variation in apparent solubility. The tests were run in numerical order,

TABLE XIII

Concentration of Tantalum from Ta-0.5% Zr Alloy in Potassium

Test No.	Temp, °C	Time, hrs.	K, gm	Ta, μgm	Ta, wppm
630	1197	4	1.75	1040	595
631	1198	1	1.60	870	543
639	1202	4	1.95	135	69
647	1203	0.5	1.95	402	206
640	1205	0.5	1.72	4425	2570
623	1222	4	1.95	9770	5000
624	1421	4	1.82	1260	700
644	1631	4	1.98	32	16

and it is seen that there is no regularity in the amount of tantalum found with test sequence. The generalization may be drawn, however, that the solubility of tantalum from this alloy is significantly greater than that from either of the more highly gettered alloys T-111 and ASTAR-811C.

Niobium-Zirconium Alloys in Potassium

The results of experiments with two niobium-zirconium alloys, Cb-1Zr commercial alloy and Nb-0.5% Zr, and Mo-1/2 Ti sample collectors, with potassium solvent, are shown in Table XIV. The data are not sufficient to show a well-defined temperature dependence. The apparent solubility of niobium from the 1% zirconium alloy is about 6 ppm in this temperature range, and that from the 0.5% alloy somewhat higher. The data suggest that the solubility is dependent to a degree on the amount of gettering constituent (Zr) in the alloy.

TABLE XIV

Concentration of Niobium from Niobium-Zirconium Alloys in Potassium

Test No.	Solute	Temp., °C	Time, hrs	K, gm	Nb, μgm	Nb, wppm
601	Cb-1Zr	1200	4	1.53	9.4	6.0
603	Cb-1Zr	1382	4	1.56	8.0	6.5
219*	Cb-1Zr	1000	8	2.27	not detected	< 1
224*	Cb-1Zr	1240	4	1.84	11	6
626	Nb-0.5Zr	1200	4	1.95	19.6	10.0
627	Nb-0.5Zr	1417	4	1.55	19.3	12.4
635	Nb-0.5Zr	1614	4	1.75	336	191

*Earlier experiments, reported in Reference (20).

Molybdenum-Zirconium Alloys in Potassium

The results of two experiments with each of two molybdenum-zirconium alloys, Mo-0.5% Zr and TZM, and Cb-1Zr sample collectors, with potassium solvent, are shown in Table XV. The data are insufficient to show more than that the commercial TZM alloy, which has 0.5% Ti as well as 0.07% Zr, is less soluble than the specially prepared 0.5% Zr alloy. Results of earlier work (Ref. (20)) show from 1.3 to 13.9 wppm Mo dissolved in potassium from pure molybdenum crucibles in the 1000-1200 °C range.

TABLE XV

Concentration of Molybdenum from Mo-Zr and Mo-Ti-Zr Alloys in Potassium

Test No.	Solute	Temp., °C	Time, hrs	K, gm	Mo, μgm	Mo, wppm
646	Mo-0.5Zr	1203	4	1.62	218	135
648	Mo-0.5Zr	1380	4	1.74	122	70
791	TZM	1410	4	2.35	25.5	15
794	TZM	1400	4	2.20	18.5	8.5

Rhenium in Potassium

The results of four experiments with a rhenium solute crucible and Cb-1Zr sample collectors, with potassium solvent, are shown in Table XVI. Rhenium was undetected at the 1 wppm level in any experiment. The actual solubility may be much below this level, which is the limit of the analytical chemistry procedure used. Rhenium is the least soluble of any solute studied in this program.

TABLE XVI

Concentration of Rhenium in Potassium

Test No.	Temp., °C	Time, hrs	K, gm	Re, μgm	Re, wppm
620	1200	4	1.95	< 2	< 1
629	1200	4	1.35	< 2	< 1
634	1415	4	1.60	< 2	< 1
643	1621	4	1.72	< 2	< 1

Hafnium in Potassium

The results of three experiments with a hafnium solute crucible and Mo-1/2 Ti sample collectors, with potassium solvent, are shown in Table XVII. The data are not sufficient to describe a temperature dependence, but it is seen that hafnium is apparently soluble in the 100 wppm range in potassium in the 1200-1400 °C temperature range.

TABLE XVII

Concentration of Hafnium in Potassium

Test No.	Temp., °C	Time, hrs	K, gm	Hf, μgm	Hf, wppm
609	1200	4	1.41	166	118
621	1373	4	1.70	175	103
641	1387	4	1.90	91	48

The exposures of the Hf samples were irregular in that when each of the capsules was opened, the crucible was found to have expanded out against the inner wall. It was necessary to machine the molybdenum capsule away from the Hf in order to recover the crucible-collector subassembly. Figure 10 shows the subassembly from Run #609 after the machining operation. This can be compared to the Hf-(Mo-0.5 Ti) weld of Fig. 11. The Hf is clearly expanded but the Mo-0.5 Ti is not. The reason for this is thought to be that during the quenching period, the capsule wall cools faster than the crucible-collector subassembly with the result that the vapor pressure of the potassium outside the crucible-collector is momentarily lower than that inside the subassembly. If the crucible is a weak material such as soft, single crystal hafnium, it cannot resist the pressure difference so it expands outward against the capsule wall. The stronger Mo-1/2 Ti does not swell. Support for this hypothesis is found in the observation that in all three Hf runs, the crucible was expanded firmly against the capsule wall.

In addition to the expansion phenomenon, the Hf crucible also appeared to be quite heavily attacked by the potassium. This attack is shown in the photograph of the interior bottom of crucible # 609 in Fig. 12. A similar surface appearance is exhibited by the walls of the crucible. Before the exposure, both the walls and the bottom had a standard machined surface. The post-test appearance suggests either that severe corrosion has taken place or that expansion of the hafnium has caused slippage along crystal planes, giving the etched appearance.

Zirconium in Potassium

The results of experiments with a zirconium solute crucible and Mo-1/2 Ti sample collectors, with potassium solvent, are shown in Table XVIII. The data are not sufficient to show the temperature dependence of apparent solubility, but they do show that many tens of wppm of zirconium will dissolve in potassium. The lowest temperature experiment (#617) shows a zirconium concentration that is anomalously high. Although the amount of potassium in the experiment was low, there was no indication of an experimental abnormality in the run.

Difficulty was encountered in making a zirconium to Mo-1/2 Ti weld. Several attempts resulted in joints that were not helium leak-tight. The zirconium crucible was damaged beyond use in these attempts, and a new zirconium rod of equal purity was obtained. The crucible made from the new zirconium was welded to a sample collector without difficulty. A swelling phenomenon similar to that described above for the hafnium crucible was noted with the

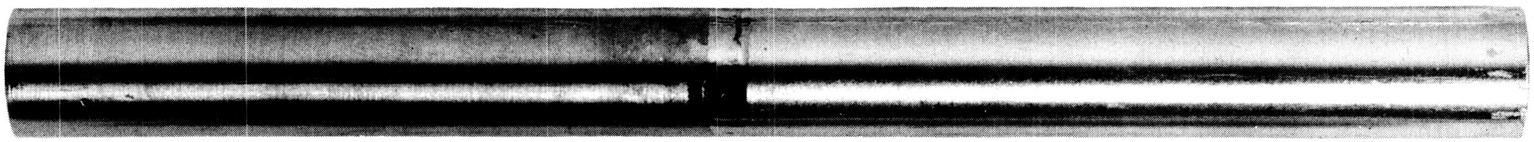


Figure 11. Hafnium-(Mo-0.5Ti) Assembly Before Exposure, One and One-Half Times Actual Size.

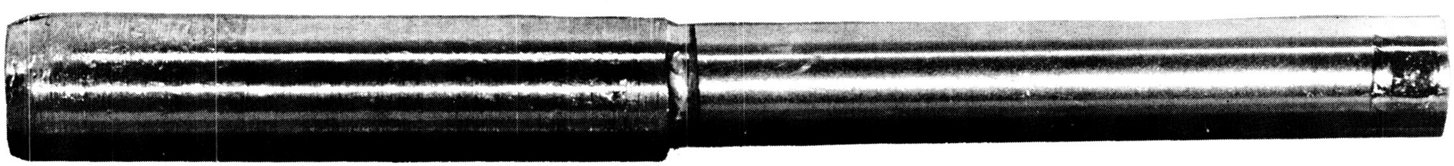


Figure 10. Hafnium-(Mo-0.5Ti) Assembly After Exposure and Machining to Remove Capsule, One and One-Third Times Actual Size.

TABLE XVIII

Concentration of Zirconium in Potassium

Test No.	Temp., °C	Time, hrs	K, gm	Zr, μgm	Zr, wppm
617	900	4	0.625	176	282
622	900	4	1.90	121	64
628	1200	4	1.70	136	80

zirconium crucible after the 1200 °C test. Figure 13 shows the appearance of the crucible-collector assembly after the swelling had occurred. As with the hafnium, this phenomenon is attributed to the combination of metal weakness and the difference in potassium pressure inside and outside the crucible-collector assembly during rapid quenching.

Figure 12. Bottom of Hafnium Crucible After Four Hours Exposure to Potassium at 1200 °C, Three Times Actual Size.

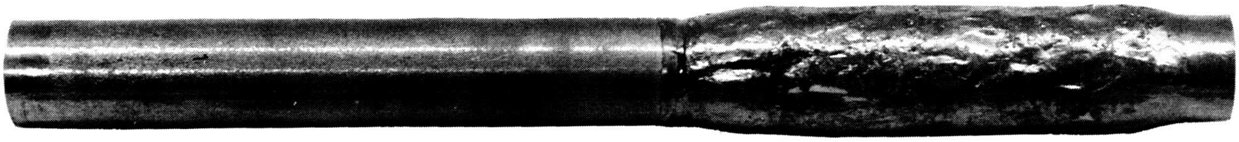


Figure 13. Zirconium-(Mo-0.5Ti) Assembly After Exposure, One and One-Quarter Times Actual Size.

Tungsten in Potassium

The results of experiments with vapor deposited tungsten crucibles and Cb-1Zr sample collectors, with potassium solvent, are shown in Table XIX. The crucible in test #406 was found to be cracked when the outer capsule was opened, but there had apparently been no loss of potassium. The results show an appreciable concentration of tungsten, much greater than that reported above for rhenium, but also much less than that reported for tantalum (20). Since it was not feasible to obtain tungsten alloys with gettering alloy additions (Zr or Hf), the only data obtained are for the high purity vapor-deposited material.

TABLE XIX

Concentration of Tungsten in Potassium

Test No.	Temp., °C	Time, hr	K, gm	W, μgm	W, wppm
406	1203	4	1.2	91	76
407	1391	4	1.5	60	40
413	1583	4	1.5	92	61

T-111 in Lithium

The results of experiments with T-111 alloy solute crucibles and Mo-$^1/_2$Ti sample collectors, with lithium solvent, are shown in Table XX. Except for one run (#714 at 11 wppm), all the results are the same within experimental and analytical uncertainty, and the solubility value of 2 to 3 wppm may be assigned for tantalum in lithium over the 1200 to 1600°C temperature range. The two preliminary experiments using less pure (gettered but not distilled) lithium, and made before the improvements in the analytical method for tantalum were done, showed that significantly more tantalum apparently dissolved. Since there are two known differences between the two groups of experiments, it is not possible to assign the apparent solubility difference to a specific cause.

TABLE XX

Concentration of Tantalum from T-111 Alloy in Lithium

Test No.	Temp., °C	Time, hr	Li, gm	Ta, µgm	Ta, wppm
717	1197	4	1.86	5.6	3
712	1202	4	3.07	< 1	< 1
719	1202	4	1.93	4.2	2
713	1203	4	2.22	< 1	< 1
729	1203	4	1.90	4	2
739	1203	1	0.54	1.5	3
740	1203	0.25	0.85	2.5	3
714	1308	4	1.20	13.5	11
730	1395	4	1.60	3	2
738	1600	4	1.10	2	2
Tests with less pure Li, and before analytical technique improvements:					
402	1363	4	0.55	11	20
401	1603	4	0.70	6.5	11

ASTAR-811C in Lithium

The results of experiments with ASTAR-811C alloy solute crucibles and Mo-½Ti sample collectors, with lithium solvent, are shown in Table XXI. All the results are the same within experimental and analytical uncertainty. The solubility value of 2 to 3 wppm for tantalum from this alloy, in lithium, may be assigned over the temperature range 1000 to 1600 °C. The composition difference between T-111 and ASTAR-811C does not seem to affect the solubility of tantalum from the alloys in lithium. The remarks concerning the experiments with less pure lithium made for the T-111 experiments above apply equally well to the two tests with ASTAR-811C under the same conditions, as seen in Table XXI.

Three experiments with ASTAR-811C, experimentally identical to those listed in Table XVIII with high purity lithium, were analyzed for hafnium content. These results are shown in Table XXII. The results are confusing, since it is seen that apparently more hafnium than tantalum dissolved from the alloy, although hafnium constitutes only about 1% by weight, whereas tantalum is about 90% by weight of the alloy. It may be conjectured that some of the hafnium is present as an oxide, since its function in the alloy is to getter oxygen, and that the lithium interacts with a portion of the oxide, permitting the hafnium to enter the solution. It is also of interest to note that the hafnium concentration found in these experiments is the same as that found for a pure hafnium solute (Table XXII). This suggests that the concentration of hafnium in the solute is not the major determining factor in the solution of hafnium in lithium. One possibility is that the major factor may be the oxygen content of the potassium which would then account for the nominal equality of the two sets of "solubility" data.

TABLE XXI

Concentration of Tantalum from ASTAR-811C Alloy in Lithium

Test No.	Temp., °C	Time, hr	Li, gm	Ta, μgm	Ta, wppm
716	1007	4	2.96	14	5
715	1233	4	1.42	4	3
731	1400	4	1.40	3	2
763	1400	4	1.60	3	2
762	1620	4	2.47	1	< 1
Tests with less pure Li, and before analytical technique improvements:					
649	1195	4	0.345	6.3	18
650	1391	4	0.325	7.5	23
720	Control at 27 μgm Ta			28	
733	Control at 9 μgm Ta			8	

TABLE XXII

Concentration of Hafnium from ASTAR-811C Alloy in Lithium

Test No.	Temp., °C	Time, hr	Li, gm	Hf, μgm	Hf, wppm
746	1203	4	0.96	11	11
757	1410	1	0.77	6	8
756	1600	4	0.78	5	6

Hafnium In Lithium

The results of experiments with a hafnium crucible and Mo-$\frac{1}{2}$Ti sample collectors, with lithium solvent, are shown in Table XXIII. The observed solubility of hafnium in lithium in the temperature range 1000 to 1400 °C is seen to be about 6 wppm.

Great difficulty was encountered in welding the hafnium crucible to the Mo-$\frac{1}{2}$Ti sample collector. After a weld was made, numerous leaks were always found both in the weld area and along the hafnium crucible. These were sealed by defocussing the electron beam and melting the surface of the hafnium in the region of the leak. After repeated leak testing and repairing the assembly would be found to be leak-tight. However, this generally required that nearly the complete surface of the hafnium be melted in the electron beam. New leaks developed after each test, so this procedure was repeated before each loading with lithium.

TABLE XXIII

Concentration of Hafnium in Lithium

Test No.	Temp., °C	Time, hr	Li, gm	Hf, μgm	Hf, wppm
759	1015	4	1.05	7.5	7
773	1200	4	1.07	6.5	6
771	1400	4	1.62	9	6
Control at 8 μgm Hf				10.3	

Molybdenum in Lithium

The results of experiments with molybdenum solute crucibles and Cb-1Zr sample collectors, with lithium solvent, are shown in Table XXIV. The scatter in the data precludes the assigning of a temperature dependence. No reason for the scatter is apparent, and the chemical analysis seems to be reliable. The best value for the apparent solubility of molybdenum in lithium over the temperature range 1200 to 1600°C is 9 ± 5 wppm.

TABLE XXIV

Concentration of Molybdenum in Lithium

Test No.	Temp., °C	Time, hr	Li, gm	Mo, μgm	Mo, wppm
779	1200	4	0.41	2.5	6
722	1192	4	2.72	44	16
775	1200	4	1.19	4.8	4
724	1390	4	2.42	16	7
727	1400	4	1.01	2	2
780	1405	4	1.1	15.3	14
749	1620	4	0.57	6	11
Control at 2 μgm Mo				2.0	

Rhenium in Lithium

The results of experiments with a rhenium solute crucible and Cb-1Zr sample collectors, with lithium solvent, are shown in Table XXV. The solubility of rhenium in lithium may be described as 1 ± 1 wppm over the temperature range 1200 to 1600°C, from these data. The same crucible was used that had been previously used for potassium solubility experiments.

TABLE XXV

Concentration of Rhenium in Lithium

Test No.	Temp., °C	Time, hr	Li, gm	Re, μgm	Re, wppm
721	1202	4	1.64	1	0.6
750	1400	4	1.86	2	1.1
754	1602	4	1.47	2.5	1.7
Control at 4 μgm Re				4.5	

Tungsten in Lithium

The results of experiments with a tungsten solute crucible and Cb-1Zr sample collectors, with lithium solvent, are shown in Table XXVI. From these data, the apparent solubility of tungsten in lithium in the temperature range 1200 to 1600°C may be described as 2 wppm. All three tests were made with the same vapor deposited tungsten crucible. However, the crucible was very brittle, and leaks developed during handling. These were satisfactorily sealed by careful electron beam melting of the surface in the leak region, as was done with the hafnium crucible.

TABLE XXVI

Concentration of Tungsten in Lithium

Test No.	Temp., °C	Time, hr	Li, gm	W, μgm	W, wppm
765	1202	4	1.15	3	2.5
758	1400	4	1.52	$<$ 1	$<$ 1
769	1610	4	1.54	4	2.5
Control at 2 μgms W				2.5	

DISCUSSION OF RESULTS

The dissolution of a refractory metal in a liquid alkali metal involves at least two processes. The first of these is the straightforward solution of the refractory metal atoms themselves, and the second involves the formation of a soluble oxygen-bearing species. Both processes will occur in every system, although in the usual case, one will dominate. Which of the two is dominant in any particular system will depend on factors such as the amount of oxygen present and the chemical stability of the pertinent oxygen-bearing species. Indeed, the "solubility" values reported for many systems of known high oxygen content (whether it be in the solvent or in the solute) are quite high, say, 100 to 1000 ppm or more at 1200°C. Apparently, the oxygen-dependent processes dominate in such systems. Much of the early solubility data has this character. In recent years, refractory metals having generally lower impurity contents have become available. In addition, the ability to purify the alkali metals used in performing solubility tests has increased, so that measurements can now be made in very highly purified systems. Nevertheless, the difficulty of removing oxygen from the refractory metals is great, and, even when extreme measures are taken to produce highly purified metals, several tens of ppm of oxygen usually remain. The degree to which a given amount of oxygen will affect a solubility measurement is then dependent upon the chemical stability of the soluble alkali metal-refractory metal-oxygen species. In such a system the oxygen will be partitioned among the alkali metal solution, the simple refractory metal oxide, and the double oxide of the alkali metal with the refractory metal. The distribution of the available oxygen will depend upon the relative chemical stabilities of 1) the alkali metal oxide, M_2^IO, dissolved in the alkali metal to form a solution of the observed oxygen concentration, 2) the refractory metal oxide MO_x at its concentration in the solution, and 3) the complex oxide $M_2^IMO_{x+1}$ at its concentration in the solution. Unfortunately, there are few data on the heats or free energies of formation of the complex oxides of potassium or lithium, and no data on the solubilities of the compounds.

It is of interest to compare the chemical stabilities in the Li-Mo-O, the K-Mo-O, and the Li-Hf-O systems, for which systems some data are available in the literature. The evaluation of the estimated free energies of formation of Li_2O and K_2O in their alkali metal melts is accomplished using the relations,

$$\Delta F_f \text{ (dissolved oxide)} = \Delta F_f \text{ (solid)} + \Delta F \text{ (solution)}$$

$$\Delta F \text{ (solution)} = RT \ln \left[\text{ppm O observed/ppm O at saturation} \right]$$

$$= RT \ln a_O.$$

The free energies of formation of the double oxides are estimated using the relation,

$$\Delta F_f(T) = \Delta H_f(298) - \Delta S_f(298)$$

As a first approximation, $\Delta S_f(298)$ can be taken as weighted average per oxygen atom of the $\Delta S_f(298)$ for the alkali metal oxide and the refractory metal oxide. The data developed in this way are shown in Table XXVII.

Based upon the values in Table XXVII, one sees that the oxygen in a lithium solution containing 33 ppm O has the very substantial chemical stability of -115.7 kcal/g atom O. In the competition for oxygen by molybdenum, say, one sees that because the stability of $MoO_3(s)$ is only -32.7 kcal/g atom O, the tendency for molybdenum to form MoO_3 in the lithium solution corresponds to a ΔF (reaction) of +83 kcal/g atom O. Therefore little reaction is expected at 1500°K. A similar comparison of the $\Delta F_f(1500)$ for Li_2MoO_4 and Li_2O dissolved in lithium shows a ΔF (reaction) of +47 kcal/g atom O for the formation of the complex compound. Again, one would expect to find that this reaction would not be an important factor in the solution of molybdenum in lithium. Unfortunately, no data are available for the compound Li_2MoO_3 in which the molybdenum is present in the +3 state rather than in the more highly oxidized +6 state found in Li_2MoO_4.

It does seem more likely that the lower valence states would be more prevalent in the highly reducing liquid metal environment. However, it is of interest to note that the molybdenum solubility values shown in Table XXIV are all in the low ppm range which is compatible with the prediction that the solubilization of molybdenum by the formation of oxygenated species is not a major factor in lithium systems.

TABLE XXVII

Thermodynamic Data for Selected Oxygen-Bearing Compounds

Compound	State	$\Delta H_f(298)$	Ref.	$\Delta S_f(298)$ estimated	$\Delta F_f(1500)$	Ref	RT log a* at 1500K	$\Delta F_f(1500)$ (solutions)
		Kcal per g atom O		e.u.	Kcal per g atom O		Kcal per g atom O	Kcal per g atom O
Li_2O	solid				- 95.4	(12)		
Li_2O	33 wppm O in Li						-20.3	-115.7
K_2O	(solid)				- 37.	(12)		
K_2O	6 wppm O in K						-29.	- 66.
MoO_3	solid				- 32.7	(7)		
HfO_2	solid				- 99.0	(7)		
ZrO_2	solid				- 96.9	(7)		
Li_2MoO_4	solid	- 91.3	(26)	-22.6	- 68.7	Calc'd		
K_2MoO_4	solid	- 89.3	(22)	-23.4	- 65.9	Calc'd		
Li_2HfO_3	solid	-141.1	(29)	-25.1	-103.5	Calc'd		

* Solubility of O in Li is extrapolated from the data of Hoffman[11] to be 30,000 wppm at 1500 °K. Solubility of O in K is extrapolated from the data of Williams et al.(27) to be 100,000 wppm at 1500 °K. Both of these values must be considered very tentative. $a_0(Li) = 33/30,000 = 1.1 \times 10^{-3}$; $a_0(K) = 6/100,000 = 6 \times 10^{-5}$.

For the case of the solution of hafnium in lithium, an examination of Table XXVII shows that the free energy of the reaction to form HfO_2 from the oxygen in lithium is +16.7 kcal/g atom O and that for the formation of Li_2HfO_3 is +12.2 kcal/g atom O. These values are much less positive than those for molybdenum, and suggest that there is a greater tendency for the reactions to occur. However, at equilibrium, HfO_2 would be expected in the solution at an activity of about 10^{-3} and Li_2HfO_3 at an activity of about 10^{-2}. Therefore, the contributions of these species (in solution) to the amount of hafnium in solution is not likely to be large. This is borne out by an examination of the data in Table XXIII, which show solubility values below 10 ppm Hf in Li containing 33 ppm O.

In potassium solutions containing 6 ppm O, the data in Table XXVII show that the free energy of reaction to form MoO_3 from the oxygen in the potassium is $|-32.7 - (-66)|$ or +33.3 kcal/g atom O at 1500°K, so that the formation of MoO_3 is not thermodynamically favored. However, the ΔF (reaction) to form the compound K_2MoO_4 is seen to be +0.1 kcal/g atom O from the values given in Table XXVII. In other words, the chemical stabilities of K_2MoO_4, and K_2O dissolved to yield 6 ppm O in liquid potassium, are essentially equal at 1500°K. Therefore, one would expect a substantial tendency for the formation of potassium molybdate, and the probable solubilization of molybdenum by this mechanism. One question that has an important bearing on the enhancement of the apparent solubility of molybdenum is that of the solubility of the molybdate compound. If the compound molecules are more soluble than are molybdenum atoms, then the observed "solubility" of molybdenum in potassium could be quite large. Further, it would be very sensitive to the oxygen content of the system. This is illustrated by the data shown in Table XV, in which the specially prepared Mo-0.5 Zr alloys show solubility values of the order of 100 ppm at 1200-1400°C. The difference between these nominal 100 ppm values and the nominal 10 ppm value at 1400°C for the TZM alloy can perhaps be ascribed to the effect of internal gettering. TZM contains about 0.6 percent of (Ti plus Zr) and is prepared under conditions which maximize the distribution of these group IV elements, so that their gettering action is maximized. The special alloy was made by co-melting the pure elements and swaging the ingot to size, but no specific effort was made to ensure that a fully homogeneous product was produced. Therefore, it is not unlikely that the effectiveness of the getter zirconium was less in the special alloy than in TZM. Therefore, the TZM is thought to show a lower solubility than molybdenum because its oxygen impurity is gettered by the titanium and zirconium, and is not readily available for solubilizing the molybdenum.

This internal gettering action of the Group IVA metals was recognized at the outset of this work and some of the alloys tested were chosen to test this hypothesis. The effects on the "solubility" value of adding increasingly larger amounts of a getter to refractory metals are shown in Table XXVIII. The data shown in Table XXVIII were measured using rather highly purified potassium so that the general reduction in apparent solubility with an increase in zirconium (or hafnium) content can be attributed primarily to the effect of the gettering additive.

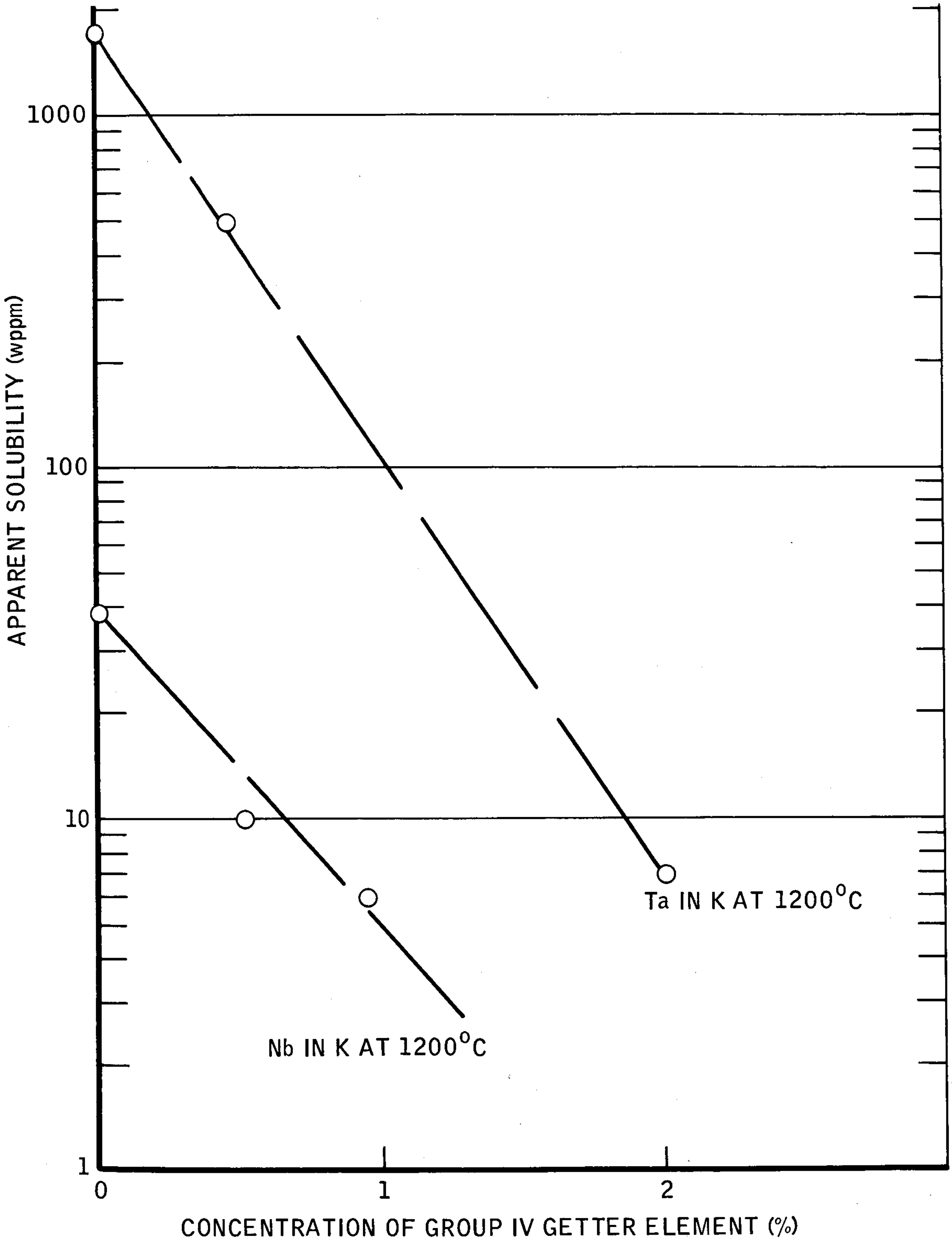


Figure 14. The Effect of Getter Concentration on the Apparent Solubility of Tantalum and Niobium in Potassium.

TABLE XXVIII

Variation in Solubility Values in 1200 °C Potassium with Getter-Concentration in Refractory Metals

Solute and Composition		Solubility wppm	Reference
Ta	single crystal	1700	(20)
Ta-0.5 Zr		(500)	This report
T-111	Ta-8W-2Hf	7	This report
ASTAR=811C	Ta-8W-1 Re-1 Hf-0.025C	7	This report
Nb	single crystal	40	(20)
Nb-0.5 Zr		10	This report
Cb-1 Zr		6	This report

TABLE XXIX

Solubility Values at 1200 °C

Lithium Solvent			
Ti	V	Cr, (40 ppm)	
Zr	Nb, (42 ppm)	Mo, 5 ppm	
Hf, 6 ppm	Ta, 2 ppm	W, 2 ppm	Re, 1 ppm
Potassium Solvent			
Ti (100 ppm)	V	Cr	
Zr, (80 ppm)	Nb, 6 ppm	Mo (8 ppm)	
Hf, (100 ppm)	Ta, 7 ppm	W	Re, < 1 ppm

When the additive level reaches about one or two percent, the effect of the getter has reduced the apparent metal solubility to a value less than 10 wppm at least in the case of Ta and Nb, as is shown in Figure 14. One would not expect to find any appreciable further reduction as the getter concentration is increased. The presumption is that at this concentration level, the zirconium has combined with the oxygen present in the alloy, and has markedly reduced its tendency to form soluble oxygen-containing species in the alkali metal. In effect, therefore, the Group IVA metal gettered Group VA or Group VIA alloy plus the purified, low-oxygen, alkali metal system is nominally equivalent to an oxygen-free system or, at least, to a very low oxygen system.

One might expect that the solubility values of Group VA and Group VIA metals measured in such systems would approach the simple metal atom solubility values, and it is interesting to compare the values for the various solutes and for each of the solvent alkali metals. The solubility values listed in Table XXIX have been chosen as being representative values for the systems at 1200°C. The values in parenthesis are estimated.

Although Table XXIX is not complete, some interesting comparisons can be made based on the interpretations of the data shown in Table XXVII. For example, the solubility values in lithium for the gettered alloys of the sixth period metals are lower than in potassium. This is in agreement with the earlier observation that the stability of Li_2MoO_4 is less than that of the oxygen (Li_2O) in the solvent lithium, and that the stability of the analogous K_2MoO_4 is equal to that of the oxygen (K_2O) in the solvent potassium. However, one must be careful in drawing too-firm conclusions about the nature of the systems from these data because of their small number and the fact that the systems were probably not in true equilibrium with respect to the distribution of the oxygen which was present in both the refractory metal and in the solvent alkali metal. However, it seems likely that in potassium, whose affinity for oxygen is comparable with those of the refractory metals, the somewhat higher solubilities may be the result of a larger contribution of the complex oxide formation and solution process.

The most striking difference in solubilities of the same metals between the lithium and the potassium solvent is in the group IVA metals. They are quite soluble (relative to other refractory metals) in potassium, but hafnium is soluble to only a modest degree in lithium. Again, this may be ascribed to the fact that the oxygen in the lithium solvent is strongly bound, and although the group IVA metals do form rather stable Li_2MO_3 compounds, their stability per gram atom oxygen is less than that of oxygen in lithium. Therefore, the simple solution process predominates. In potassium, however, the K_2MO_3 compounds are more nearly equal in stability to the oxygen in potassium so that the formation and (presumed) solution of these compounds in potassium does contribute in a major way to the observed solubilities.

In summary, the "solubility" values found for a given refractory metal decrease as the effective oxygen activity in the system decreases; the solubility values for elements in a given period are in general inversely related to their melting points; and the simple, atomic "solubility" values for the Group VA and VIA metals and for rhenium are typically in the low ppm or fractional ppm range.

CONCLUSIONS

A limited number of measurements of the solubility of refractory transition metals and alloys in potassium and in lithium have been made. In general, the solubilities of these elements are larger in potassium than in lithium. This is ascribed to the greater contribution to the observed solubilities in potassium of the formation and the solution of complex alkali metal-refractory metal-oxygen compounds. This mechanism is less prevalent in lithium solutions containing low oxygen concentrations because of the significantly greater tendency for oxygen (Li_2O) to remain dissolved in dilute solution in lithium.

APPENDIX A

ANALYTICAL PROCEDURES

The analytical procedures for the determinations of the various solute materials studied in the program are given in this appendix. In most cases, the procedures are based on published procedures, but with alterations and added steps which have been found necessary to adapt them to the low levels of solute concentrations, and the need to prevent interferences caused by the presence of other solute materials. Because the solutes of interest were frequently found to be present in the few ppm range, and because the detection limits of many of the procedures are also in the few ppm range, it was frequently necessary to perform analyses using 'spiked' samples. In such cases, a few micrograms of the solute were added to the test sample aliquots to ensure that the solution being analyzed would show the presence of at least the detection limit level of the solute. Corrections for the spike levels of solutes were made in the reported analytical results, of course.

1. SAMPLE PREPARATION FOR POTASSIUM SAMPLES

Each potassium and solute sample delivered for analysis was contained in the collector end of the crucible-collector subassembly used in the test exposure. The collector with the frozen potassium was cut with a tubing cutter from the crucible in a recirculating inert atmosphere glove box. The potassium was melted, and poured into a 50 ml Vycor crucible. This crucible was removed from the glove box and was placed in the dissolver apparatus shown in Fig. 15, in which the potassium was reacted slowly and dissolved in water vapor carried in the argon gas stream. After the potassium had dissolved, the solution was acidified with concentrated HCl.

The potassium remaining on the solubility test collector wall was carefully dissolved in water, and the collector was rinsed with HCl. This rinsing solution is added to that obtained in the dissolver.

The collector was then etched to dissolve any of the solute which may have deposited on the wall of the collector. The etchant solution used depended upon the solute and collector materials involved and is defined for each solute in the individual procedure described below. In all cases, the etch washings were added to the metal dissolution solution to produce a single aqueous sample containing all the solute and all of the potassium.

2. DETERMINATION OF ZIRCONIUM IN POTASSIUM

a. Principle

Zirconium is extracted with tri-n-octylphosphine oxide (TOPO) from a 7$\underline{M}$ solution of nitric acid with the color being developed in the organic phase using pyrocatechol violet in the presence of pyridine.

b. Apparatus

Beckman Spectrophotometer, Model DU.

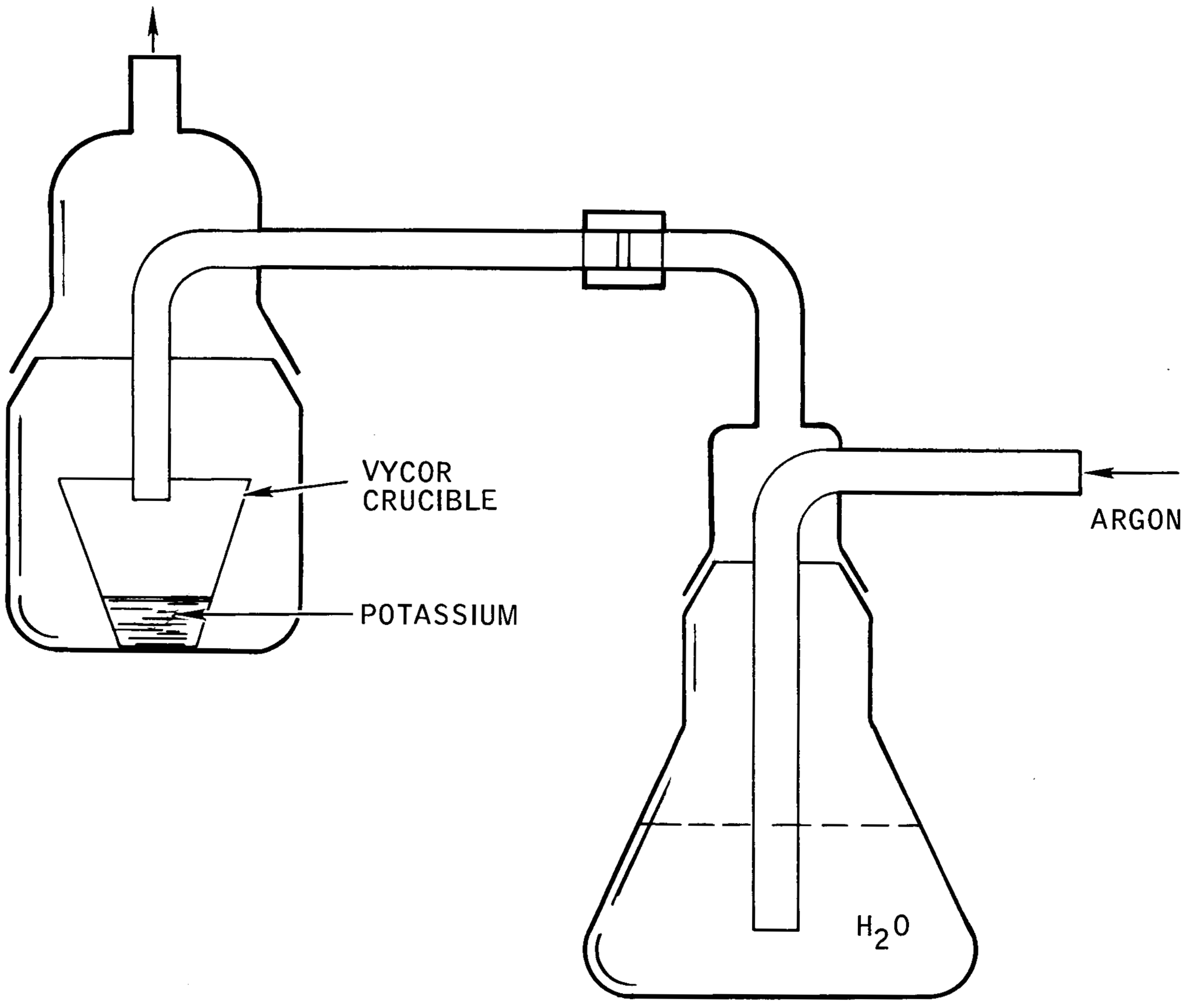


Figure 15. Dissolver Apparatus for Potassium.

c. Reagents

1) Standard zirconium solution: Dissolve 100 mg of pure Zr metal in 10 ml of HF and a few drops of HNO_3 and dilute to 100 ml. Make subsequent dilutions with 1:99 HF.

2) Tri-n-octylphosphine oxide (TOPO), 0.1M: Dissolve 1.93g TOPO in 50 ml cyclohexane. Prepare daily.

3) Pyrocatechol violet: 0.05% in absolute ethanol. Prepare immediately before use.

4) Boric acid, H_3BO_3, 5%.

5) Perchloric acid, $HClO_4$, 70%.

6) Nitric acid, HNO_3, 16N.

7) Hydrofluoric acid, HF, 27N.

8) Ethanol, absolute.

9) Pyridine, reagent grade.

d. Procedure

The potassium samples containing the zirconium solutes were dissolved in the manner described in Section 1. The collectors were rinsed with 27 N HF and water, and the washings were combined with the original solution.

Pipette aliquots containing 4 to 50 μg Zr into Teflon beakers. Add five ml H_3BO_3, 1 ml $HClO_4$, and 1 ml HNO_3 to each sample and evaporate to dryness. Repeat the addition of the H_3BO_3, $HClO_4$, and HNO_3 and the evaporation step twice. Add 12 ml HNO_3 and transfer the samples to 60 ml separatory funnels. Dilute to 25 ml with H_2O. Shake the solution for 15 minutes with 5 ml of the TOPO reagent. Transfer 2 ml of the organic layer to a dry 25 ml volumetric flask. Add 10 ml absolute ethanol, 2 ml pyrocatechol violet, and 5 ml pyridine. Then dilute to volume with absolute ethanol and allow to stand for five minutes. Read the absorbance in a spectrophotometer at 655 nm* against a reagent blank in 2 or 5 cm absorption cells.

The calibration curve is obtained by treating 3 to 50 μg Zr in the same matrix as the samples in the manner described above.

e. Discussion

The methods of Young and White (29) and of Wood and Jones (28) have been modified to suit the specific needs of the determination of Zr in potassium. The fuming of the samples with H_3BO_3, HNO_3, and $HClO_4$ serves a twofold purpose by oxidizing the molybdenum to Mo(VI) and eliminating the fluoride ion. Mo(VI) is not extracted into TOPO from nitric acid solution.

---

*nm = nanometer (10^{-9} meter)

3. DETERMINATION OF HAFNIUM IN POTASSIUM

a. Principle

Hafnium is extracted with TOPO from a 7M solution of nitric acid with the color being developed in the organic phase using pyrocatechol violet in the presence of pyridine.

b. Apparatus

Beckman Spectrophotometer, Model DU.

c. Reagents

1) Standard hafnium solution: Dissolve 100 mg of pure Hf metal in 10 ml of HF and a few drops of HNO_3, and dilute to 100 ml. Make subsequent dilutions with 1:99 HF.

2) Tri-n-octylphosphine oxide (TOPO), 0.1M: Dissolve 1.93g TOPO in 50 ml cyclohexane. Prepare daily.

3) Pyrocatechol violet: 0.05% in absolute ethanol. Prepare immediately before use.

4) Boric acid, H_3BO_3, 5%.

5) Perchloric acid, $HClO_4$, 70%.

6) Nitric acid, HNO_3, 16N.

7) Hydrofluoric acid, HF, 27N.

8) Ethanol, absolute.

9) Pyridine, reagent grade.

d. Procedure

The potassium samples containing the hafnium solutes were dissolved in the manner described in Section 1. The collectors were rinsed with 27N HF and water, and the washings were combined with the original solution.

Pipette aliquots containing 4 to 70 µg Hf into Teflon beakers. Add 5 ml H_3BO_3, 1 ml $HClO_4$, and 1 ml HNO_3 to each sample and evaporate to dryness. Repeat the addition of the H_3BO_3, $HClO_4$, and HNO_3 and the evaporation step twice. Add 12 ml HNO_3 and transfer the samples to 60 ml separatory funnels. Dilute to 25 ml with H_2O. Shake the solution for 15 minutes with 5 ml of the TOPO reagent. Transfer 3 ml of the organic layer to a dry 25 ml volumetric flask. Add 10 ml absolute ethanol, 2 ml pyrocatechol violet, and 5 ml pyridine. Then dilute to volume with absolute ethanol and allow to stand for 5 minutes. Read the absorbance in a spectrophotometer at 655 nm against a reagent blank in 2 or 5 cm absorption cells.

The calibration curve is obtained by treating 3 to 50 ug Hf in the same matrix as the samples in the manner described in the procedure.

e. Discussion

The methods of Young and White (29) and of Wood and Jones (28) have been modified to suit the specific needs of the determination of Hf in potassium. The fuming of the samples with H_3BO_3, HNO_3, and $HClO_4$ serves a twofold purpose by oxidizing the molybdenum to Mo(VI) and eliminating the fluoride ion. Mo(VI) is not extracted into TOPO from nitric acid solution.

4. DETERMINATION OF NIOBIUM IN POTASSIUM

a. Principle

Niobium forms a purple-colored complex with 4-(2-pyridylazo)-resorcinol (PAR) in an acetate buffered-EDTA medium at pH 5.8. One µg Nb can be determined in the presence of 200 mg K and 1000 µg Mo.

b. Apparatus

Beckman Spectrophotometer, Model DU.

c. Reagents

1) Niobium Standard. Dissolve 100 mg pure niobium metal in concentrated HF plus a few drops of HNO_3. Prepare dilutions with 1:99 HF.

2) PAR reagent. Completely wet 0.295g 4-(2-pyridylazo)-resorcinol with 2 ml of 5% NaOH and dilute to one liter with water. Prepare daily.

3) Buffer Solution, pH 5.8. Dissolve 80g of ammonium acetate in H_2O, add 6.5 ml of glacial acetic acid and dilute to one liter with water.

4) EDTA, Disodium ethylene diaminetetra-acetate, 0.02<u>M</u>.

5) Hydrofluoric acid, HF, 1:99.

6) Boric acid, H_3BO_3, 4%.

7) Hydrochloric acid, HCl, 12<u>N</u>.

8) Hydrofluoric acid, HF, 27<u>N</u>.

9) Nitric acid, HNO_3, 16<u>M</u>.

10) Perchloric acid, $HClO_4$, 70%.

11) Ammonium hydroxide, NH_4OH, 1:1.

d. Procedure

The potassium sample containing the niobium solute was melted and dissolved in the manner described in Section 1. For the determination of niobium, the collector was rinsed as follows: 12<u>N</u> HCl, H_2O, 27 <u>N</u> HF, and finally water. All rinses were combined with the original solution.

Pipette aliquots containing 1 to 5 μg Nb into 50 ml Teflon beakers, add 1 ml HNO_3 and 0.5 ml of $HClO_4$. Evaporate the solution to dryness. Warm the residue with 2 ml dilute HF and a few drops of water to dissolve the salts. Then add 10 ml EDTA, 5 ml H_3BO_3, and adjust the pH to approximately 6 with NH_4OH. Add 15 ml PAR, and 5 ml buffer solution. Transfer the solution to 50 ml volumetric flasks and add 15 ml PAR and 5 ml buffer solution. Let stand for one hour, dilute to volume, and read the absorbance in a spectrophotometer at 550 nm in 10 cm absorption cells against a reagent blank.

For aliquots of samples containing 10-70 μg of niobium, the steps involving the evaporation with HNO_3 and $HClO_4$ and the dissolution with dilute HF are the same as described in the procedure for the 1 to 5 μg Nb samples. Then add 10 ml of EDTA and 5 ml H_3BO_3 to the dissolved salts and adjust the pH to 6 with NH_4OH. Transfer the solutions to 100 ml volumetric flasks and add 20 ml PAR and 10 ml of buffer solution. Let stand for one hour, dilute the solutions to volume and read at 550 nm in 2 or 5 cm absorption cells.

Calibration curves are constructed by treating standards prepared in similar matrices in the same manner as the samples.

e. Discussion

The method of Belcher et al. (1) was modified to determine small amounts of Nb in the presence of potassium salts and molybdenum. It was found that more PAR reagent was required than was indicated by Belcher et al. Also, by using less volume and 10 cm absorption cells, more sensitivity was obtained. It is possible to determine 0.02 μg Nb/ml of final volume without separation from the potassium salts.

5. DETERMINATION OF TANTALUM IN POTASSIUM

a. Principle

Tantalum forms a bright red complex with phenylfluorone in a slightly acid solution. Interference from some metals present as impurities is avoided by a preliminary extraction of the tantalum with hexone from a solution 0.4M HF-6M HCl. EDTA is added to complex co-extracted metals and aluminum chloride is added to complex the fluoride ion. This procedure is an adaptation of Hill's (9) and Luke's (18) methods.

b. Apparatus

1) Beckman Spectrophotometer, Model DU.

2) Cary Recording Spectrophotometer, Model 15.

c. Reagents

1) Phenylfluorone solution: Dissolve 10 mg of phenylfluorone in 4 to 5 drops of 12M hydrochloric acid and 10 ml ethanol. Dilute to 100 ml with ethanol. Prepare daily.

2) Methyl isobutyl ketone (Hexone): Add a few pellets of sodium hydroxide to methyl isobutyl ketone and redistill, discarding low boiling and high boiling fractions. Equilibrate the hexone by shaking 200 ml of hexone with 100 ml of HF-HCl wash solution.

3) EDTA solution: Dissolve 100g of disodium ethylene diaminetetra-acetate in 1 liter of water and filter the solution.

4) Standard Tantalum Solution, 1 ml = 1000 μg: Dissolve 100 mg tantalum metal in hydrofluoric acid with the aid of a few drops of nitric acid. Dilute to 100 ml in such a way that the solution will be 4M in HF. Prepare dilutions that are 0.4M in hydrofluoric acid and 6M in HCl.

5) Hydrofluoric acid, HF, 4.0M.

6) Hydrofluoric acid - hydrochloric acid wash solution: Dilute 100 ml of 4.0M hydrofluoric acid and 500 ml 12M hydrochloric acid to one liter with water. Store in polyethylene container.

7) Buffer solution: Mix 500g ammonium acetate, 700 ml of glacial acetic acid and 500 ml water. Add 2g of benzoic acid in 20 ml methanol and dilute to two liters. Dissolve 10 grams of Knox gelatin in 1 liter of hot water, cool and mix the two solutions. Adjust the pH to 4.5 with ammonium hydroxide or acetic acid.

8) Aluminum chloride solution, $AlCl_3$, 7% solution.

9) Ethanol, absolute.

c. Procedure

The potassium samples containing the tantalum solute were dissolved in the manner described in Section 1. The collectors were rinsed with 4M HF and the final solution was made 0.4M in HF and 6M in HCl when diluted to 100 ml.

Transfer aliquots of the sample solution to separatory funnels and extract with 5 ml of hexone for 10 minutes. Allow the phases to separate completely and discard the aqueous phase. Shake the hexone layer with 5 ml of the HF-HCl wash solution for one minute and discard the aqueous phase. Add 2 ml of water without shaking, then separate and discard it. Repeat the water wash to remove acid from the stopcock. Add 5 ml each of EDTA and buffer solutions by pipet to the hexone solution and shake for ten minutes to strip the tantalum from the organic phase into the aqueous phase. Add one ml of ethanol to break up the emulsion. Allow the phases to separate (15-30 min.). Collect the aqueous phase in a 25 ml volumetric flask. Wash the hexone layer twice with small portions of buffer solution and transfer the washings to the volumetric flask. Add 3 ml of the aluminum chloride and 5 ml of the phenylfluorone reagents to the volumetric flasks and mix well after each addition. Dilute the solutions in the flasks to volume with buffer solution, mix and allow to stand for one hour.

Measure the absorbance in 2 cm path length absorption cells at 530 nm on a spectrophotometer using a reagent blank as a reference.

Obtain a calibration curve by measuring 0.10 µg of Ta into a solution that is 0.4M in HF and 6M in HCl and which has the same total volume in the separatory funnels as the samples. The rest of procedure is performed in the same manner as is described for the samples.

d. Discussion

Interference due to potassium could not be detected, but 200 µg or more of Mo appeared to cause a positive bias. In order to overcome any bias that the minor constituents of the samples may cause, determine the standard calibration curves by duplicating the conditions that exist in the samples.

6. DETERMINATION OF MOLYBDENUM IN POTASSIUM

a. Principle

Molybdenum(VI) forms a green complex with toluene -3, 4 dithiol in 1N sulfuric acid. Ferrous sulfate accelerates the formation of the molybdenum dithiol complex, while citric acid complexes tungsten and prevents its reaction with dithiol at room temperature.

b. Apparatus

Beckman Spectrophotometer, Model DU.

c. Reagents

1) Dithiol reagent: Dissolve 1g toluene -3, 4 dithiol in 100 ml 0.25M NaOH solution.

2) Ferrous sulfate, $FeSO_4$, 1% in 0.2N H_2SO_4.

3) Sulfuric acid, H_2SO_4, 6N.

4) Citric acid, 50%.

5) Phosphoric acid, H_3PO_4, 85%.

6) Boric acid H_3BO_3, 4%.

7) Hydrofluoric acid, HF, 27N.

d. Procedure

The potassium samples containing the molybdenum solute were received in Cb-1% Zr collectors, and were dissolved in the manner described in Section 1. The Cb-1% Zr collectors were rinsed with water and HF and the rinsings combined with the original solution.

Transfer sample aliquots containing 2-20 µg Mo to Teflon beakers and evaporate to near dryness. Add 5 ml of H_2SO_4 and transfer to a 60 ml separatory funnel. Add the following reagents in order, and with mixing after each addition: 5 ml $FeSO_4$, 1 ml citric acid, 3 drops H_3PO_4, and 5 ml H_3BO_3. Dilute to 25 ml and add 3 ml of the dithiol reagent and mix well.

Let the solution stand for two hours, and then extract the molybdenum - dithiol complex with 10 ml of iso-amyl acetate. Repeat the extraction with 5 ml of the iso-amyl acetate. Transfer the combined iso-amyl acetate extracts to a dry 25 ml volumetric flask. Dilute to volume with iso-amyl acetate and read on a spectrophotometer against a reagent blank in 5 cm path length absorption cells at 670 nm. A calibration curve is constructed by treating 2-20 μg Mo in the same matrix as the samples and in the manner described in the procedure.

e. Discussion

It has been determined experimentally that 400 mg K and 1000 μg Nb do not interfere in this procedure. The method is essentially that of Sandell (23) except for the addition of boric acid, which is needed to complex the fluoride ion.

7. DETERMINATION OF TUNGSTEN IN POTASSIUM

a. Principle

Toluene -3, 4-dithiol forms a greenish blue complex with tungsten in the presence of titanous sulfate in strong hydrochloric acid solution. The complex is extracted into chloroform.

b. Apparatus

Beckman Spectrophotometer, Model DU.

c. Reagents

1) Titanous sulfate: (4 mg Ti/ml). Dissolve 1g titanium metal in 175 ml water and 25 ml 36N H_2SO_4. Heat in boiling water bath until the metal is dissolved. Cool, and dilute to 250 ml with water. Prepare fresh daily.

2) Dithiol reagent: Dissolve 1g toluene -3, 4-dithiol in 250 ml 0.25N sodium hydroxide. Add 1 ml thioglycolic acid. Prepare fresh daily.

3) Nitric acid, HNO_3, 2N.

4) Hydrofluoric acid, HF, 27N.

5) Hydrochloric acid, HCl, 12N.

6) Sulfuric acid, H_2SO_4, 36N.

7) Carbon tetrachloride, CCl_4, reagent grade.

d. Procedure

The potassium sample containing the tungsten solute was melted and dissolved in the manner described in Section 1. For the determination of tungsten, the collector was rinsed in sequence with: H_2O, 12N HCl, H_2O, 27N HF, and 2N HNO_3. All solutions were combined with the original sample.

Add 5 ml of sulfuric acid to aliquots of the sample and evaporate to dense white fumes. Add 10 drops of nitric acid and fume the samples again. Add the following reagents in order, with mixing after each addition: 25 ml $Ti_2(SO_4)_3$; 20 ml HCl and 10 drops HF. Heat the samples in a water bath 80-90°C) for five minutes and add 10 ml dithiol reagent and 10 drops HF. Cool, transfer to a separatory funnel using 10 ml CCl_4 and extract for two minutes. Transfer the organic phase to 25 ml volumetric flasks and repeat the extraction using 5 ml CCl_4. Combine the organic extract solutions and dilute to volume with CCl_4. Read the absorbance of the samples against carbon tetrachloride in absorption cells having a 5 cm path length, at 640 nm.

e. Discussion

It was determined experimentally that niobium and potassium do not interfere with the determination of tungsten. The method developed was based on that reported by Hobart and Hurley (10).

8. DETERMINATION OF RHENIUM IN POTASSIUM

a. Principle

Rhenium is extracted into chloroform as the tetraphenylarsonium complex. In the chloroform solution, the addition of aqueous furil dioxime and stannous chloride reagent forms a rhenium furil dioxime complex in the aqueous layer. The rhenium complex is then re-extracted into the chloroform layer.

b. Apparatus

Beckman Spectrophotometer, Model DU.

c. Reagents

1) Furil dioxime-stannous chloride reagent: 0.7g of the salt dissolved in 5 ml acetone and diluted to 80 ml with 10% $SnCl_2$.

2) Tetraphenylarsonium chloride, (TPAC) 0.1%.

3) Hydrochloric acid, HCl, 12N.

4) Hydrofluoric acid, HF, 27N.

5) Nitric acid, HNO_3, 2N.

6) Citric acid, 10%.

7) Sodium hydroxide NaOH, 10%.

8) Sodium bicarbonate, $NaHNO_3$, 10%.

9) Potassium permanganate, $KMnO_4$, 1%.

10) Stannous chloride, $SnCl_2$, 10% dissolve 10g $SnCl_2$ in 10 ml concentrated HCl and dilute to 100 ml with H_2O.

11) Acetone, Reagent grade.

12) Chloroform, $CHCl_3$, Reagent grade.

d. Procedure

The potassium containing the rhenium solute was melted and dissolved in the manner described in Section 1. For the determination of rhenium the collector was treated with a series of rinses as follows: 12N HCl, H_2O, 27N HF, H_2O, 2N HNO_3, and H_2O. The rinse solutions were all combined with the original solution.

Evaporate samples containing 0 to 50 µg Re to dryness. Dissolve the residues in the minimum amount of water required for complete dissolution, and add 0.5 ml citric acid and 5 ml $NaHCO_3$. Adjust the pH to 8-9 with NaOH solution. Add 2 ml of tetraphenylarsonium chloride and transfer the samples to 60 ml separatory funnels. Shake the solutions for three minutes with 10 ml chloroform. Drain the chloroform layer into a clean separatory funnel, wash the aqueous phase with 3 ml of chloroform, and combine the chloroform solutions. Discard the aqueous phase. Add 3 to 4 ml H_2O and one drop of $KMnO_4$ to the combined chloroform solutions, and mix by shaking. Add 10 ml of furil dioxime reagent and shake the solutions for five minutes. Then add 5 ml of acetone and shake until the aqueous layer becomes clear. Drain the chloroform layer from the separatory funnel into a 25 ml volumetric flask containing 5 ml of acetone. Rinse the aqueous phase with 3 ml of chloroform. Combine the chloroform solutions, dilute to 25 ml with acetone and allow to stand for one hour. Measure the absorbance in a spectrophotometer at 532 nm against a reagent blank in absorption cells with path length of 2 or 5 cm.

The calibration curve was obtained by treating 0 - 50 µg of Re standards in the same manner described for the samples.

e. Discussion

It was determined experimentally that 400 mg of K and 1000 µg Nb had no effect on the determination of the rhenium. The procedure was carried out as defined by Landrum and Henicksman (16), except for the additional evaporation step which was needed to remove an excess of HF.

9. SAMPLE PREPARATION FOR LITHIUM SAMPLES

Each lithium sample as received by the analytical laboratory was contained in the collector used in the test exposure. The collector containing the lithium was submerged in water in a flask with argon flowing over the water. When the reaction was complete, the lithium hydroxide solution was neutralized with hydrochloric acid and the collector was rinsed with a rinse acid appropriate for the solute being analyzed. The rinse solutions were added to the acidified solution obtained from the metal dissolution. The particular rinse acid used for each solute is described in the procedure for that solute.

10. DETERMINATION OF HAFNIUM IN LITHIUM

a. Principle

Hafnium was present in the dissolved lithium sample as hafnium fluoride. The hafnium was converted to hafnium sulfate by fuming with concentrated sulfuric acid. The hafnium sulfate was converted to hafnium "hydroxide" (probably finely divided hydrous oxide), which was carried on $Fe(OH)_3$. The hafnium was then determined by x-ray spectrography using a platinum target tube. Lutetium was added as an internal standard before the sample was fumed and the ratio of the hafnium peak height to the lutetium peak height was evaluated.

b. Apparatus

General Electric Vacuum X-ray Spectrograph with Platinum Target Tube.

c. Reagents

1) Standard lutetium solution: Dissolve 114 mg of Lu_2O_3 in a few ml of concentrated HNO_3 and dilute to 100 ml with water. This solution contains 1 mg Lu/ml. Dilute with water to obtain a concentration of 5 μg/ml.

2) Standard hafnium solution: Dissolve 100 mg of pure Hf metal in 10 ml of HF and a few drops of HNO_3, and dilute to 100 ml. Dilute with 1:99 HF to obtain a concentration of 2 μg Hf/ml.

3) Ferric chloride, $FeCl_3$, 1 mg Fe/ml.

4) Hydrofluoric acid, HF, 4<u>N</u>.

5) Sulfuric acid, H_2SO_4, 36<u>N</u>.

6) Ammonium hydroxide, NH_4OH, concentrated, 28%.

7) Ammonium hydroxide, NH_4OH, dilute, 0.1<u>M</u>.

d. Procedure

The lithium samples containing the hafnium solute were received in Mo-0.5 Ti collectors. The lithium was dissolved from the collectors with water and acidified with hydrochloric acid as described in Section 9. The collectors were rinsed with 4<u>N</u> HF, the rinsings were combined with the dissolved metal solution and the combined solution was diluted to 100 ml.

Pipette an aliquot of the sample into a 100 ml beaker and add 5 ml $FeCl_3$, 1 ml lutetium standard solution (internal standard), and 5 ml of concentrated sulfuric acid. Boil the sample to dense white fumes of H_2SO_4 and nearly to dryness. Dissolve the sample in water, transfer to a 40 ml centrifuge tube and form a precipitate with concentrated NH_4OH. Centrifuge. Wash the precipitate with dilute NH_4OH and water, dry overnight at 110°C. Analyze the $Fe(OH)_3$ precipitate containing the hafnium and lutetium by x-ray spectrography using a platinum target tube.

The x-ray instrumentation to be employed in the analysis includes a platinum target x-ray tube operated at 50 KV and 40 ma; a LiF analyzing crystal, a scintillation detector, and a pulse height analyzer set to accept the $L\alpha$ lines of Hf and Lu. These peaks are scanned at a change in rate of 2θ of 0.4° per min. with a time constant of 8 seconds. The height above background for each of these peaks is tabulated for all samples and standards, and the ratio of Hf peak height to Lu peak height is calculated. This ratio is plotted against µg Hf for the standards and is used to calibrate the samples.

A series of hafnium standards containing 0 to 20 µg Hf, 5 µg Lu, 1000 µg Mo and 500 mg Li is run simultaneously with the samples.

e. Discussion

Molybdenum and lithium do not affect the determination of the hafnium. The efficiency of the hafnium precipitation, as determined by performing the precipitation as described in the procedure and using a hafnium-181 tracer was found to be > 98%.

11. DETERMINATION OF TANTALUM IN LITHIUM

a. Principle

Tantalum forms a bright red complex with phenylfluorone in a slightly acid solution. Interference from some metals present as impurities is avoided by a preliminary extraction of the tantalum with hexone from a solution 0.4M HF-6M HCl. EDTA is added to complex co-extracted metals and aluminum chloride is added to complex the fluoride ion. This is an adaptation of the methods of Hill (9) and of Luke (18).

b. Apparatus

1) Beckman Spectrophotometer, Model DU.

2) Cary Recording Spectrophotometer, Model 15.

c. Reagents

1) Phenylfluorone solution: Dissolve 10 mg of phenylfluorone in 4 to 5 drops of 12M hydrochloric acid and 10 ml ethanol. Dilute to 100 ml with ethanol. Prepare daily.

2) Methyl isobutyl ketone (Hexone): Add a few pellets of sodium hydroxide to methyl isobutyl ketone and redistill, discarding low boiling and high boiling fractions. Equilibrate the hexone with 100 ml of HF-HCl wash solution.

3) EDTA solution: Dissolve 100g of disodium ethylene diaminetetra-acetate in 1 liter of water and filter the solution.

4) Standard tantalum solution: 1 ml = 1000 µg. Dissolve 100 mg tantalum metal in hydrofluoric acid with the aid of a few drops of nitric acid. Dilute to 100 ml in such a way that the solution will be 4M in HF. Prepare dilutions that are 0.4M in hydrofluoric acid and 6M in HCl.

5) Hydrofluoric acid, HF, 4M.

6) Hydrofluoric acid - hydrochloric acid wash solution: Dilute 100 ml of 4.0M hydrofluoric acid and 500 ml 12M hydrochloric acid to one liter with water. Store in polyethylene container.

7) Buffer solution: Mix 500g ammonium acetate, 700 ml of glacial acetic acid and 500 ml water. Add 2g of benzoic acid in 20 ml methanol and dilute to two liters. Dissolve 10 grams of Knox gelatin in 1 liter of hot water, cool and mix the two solutions. Adjust the pH to 4.5 with ammonium hydroxide or acetic acid.

8) Aluminum chloride solution, $AlCl_3$, 7% solution.

9) Ethanol, absolute.

d. Procedure

The lithium samples containing the tantalum solute were received in Mo-1/2 Ti collectors. The lithium was dissolved from the collectors in accordance with the procedure described in Section 9. The collector was rinsed with 4M hydrofluoric acid. The final solution was made 0.4M in hydrofluoric acid and 6M in hydrochloric acid and diluted to 100 ml.

Transfer an aliquot of the sample solution to a separatory funnel and extract with 5 ml of hexone for 10 minutes. Allow the phases to separate completely and discard the aqueous phase. Shake the hexone layer with 5 ml of the HF-HCl wash solution for one minute and discard the aqueous phase. Add 2 ml of water without shaking, separate, and discard the aqueous phase. Repeat the water wash to remove acid from the stopcock. Add 5 ml each of EDTA and buffer solutions by pipette to the hexone solution and allow to shake for 10 minutes to strip the tantalum from the organic phase into the aqueous phase. Add one ml of ethanol to break up the emulsion. Allow the phases to separate (15-30 min.). Collect the aqueous phase in a 25 ml volumetric flask. Wash the hexone layer twice with small portions of buffer solution and transfer the washings to the volumetric flask. Add 3 ml of the aluminum chloride and 5 ml of the phenylfluorone reagents to the volumetric flasks with buffer solution. Mix and allow to stand for one hour.

Measure absorbance in 2 cm path length absorption cells at 530 nm on a spectrophotometer against a reagent blank as a reference.

Prepare a calibration curve by measuring 0 to 10 μg of Ta into a solution that is 0.4M in HF and 6M in HCl and which had the same total volume in the separatory funnels as the samples. The rest of procedure is performed in the same manner as is described for the samples.

e. Discussion

Interference due to lithium could not be detected. However, 200 μg or more of Mo appeared to cause a positive bias. In order to overcome any bias that the constituents of the samples may cause, the standard calibration curves are determined by duplicating the conditions that exist in the samples.

12. DETERMINATION OF MOLYBDENUM IN LITHIUM

a. Principle

Molybdenum(VI) forms a green complex with toluene-3, 4 dithiol in 1N sulfuric acid. Ferrous sulfate accelerates the formation of the molybdenum-dithiol complex while citric acid complexes tungsten and prevents its reaction with the dithiol at room temperature.

b. Apparatus

Beckman Spectrophotometer, Model DU.

c. Reagents

1) Dithiol Reagent: Dissolve 1g toluene-3, 4 dithiol in 250 ml of 0.25N NaOH. After dissolution add 1 ml thioglycolic acid. Prepare daily.

2) Molybdenum Standard: Dissolve 100 mg pure molybdenum metal in 10 ml 1:1 HNO_3 and dilute to 100 ml with H_2O. For specific standards dilute aliquots of the stock solution with 0.1N HNO_3.

3) Ferrous sulfate, $FeSO_4$, 1% in 0.2N H_2SO_4.

4) Sulfuric acid, H_2SO_4, 6N.

5) Phosphoric acid, H_3PO_4, 85%.

6) Nitric acid, HNO_3, 2N.

7) Formic acid, HCOOH, Reagent Grade.

8) Citric acid, 50%.

9) Iso-amyl acetate, Reagent Grade.

d. Procedure

The lithium samples containing the molybdenum solute were received in Cb-1% Zr collectors. The lithium was dissolved from the collectors as is described in Section 9. For the determination of molybdenum, the collectors were rinsed with water and with hot 2N HNO_3, and the combined solution was then diluted to 100 ml with water.

Boil an aliquot of the sample with formic acid to remove the oxides of nitrogen, and transfer to separatory funnels. Add the following reagents in order, and with mixing after each addition: 5 ml sulfuric acid, 1 ml ferrous sulfate, 1 ml citric acid, and 4 drops H_3PO_4. Dilute to 25 ml with water, add 5 ml dithiol reagent, allow the solution to stand for two hours, and then extract with 15 ml iso-amyl acetate. Extract again with 5 ml iso-amyl acetate and combine. Transfer the iso-amyl extract to a 25 ml volumetric flask, dilute to volume with iso-amyl acetate, and read against iso-amyl acetate at 670 nm in 5 cm absorption cells.

The calibration curve was obtained by pipetting 0-10 μg of molybdenum into separatory funnels and following the procedure as outlined.

e. Discussion

It was determined experimentally that nitrate interferes with the development of the molybdenum by destroying the dithiol reagent. Lithium at the 300 mg level, niobium at the 1000 μg level, and tungsten at the 50 μg level have no effect on the determination of molybdenum by the dithiol procedure. The method was based on that reported by Sandell (23).

13. DETERMINATION OF TUNGSTEN IN LITHIUM AND NIOBIUM

a. Principle

Toluene -3, 4-Dithiol forms a greenish blue complex with tungsten in the presence of titanous sulfate in strong hydrochloric acid solution. This complex is extracted into chloroform for analysis.

b. Apparatus

Beckman Spectrophotometer, Model DU.

c. Reagents

1) Titanous sulfate, (4 mg Ti/ml): Dissolve 1g titanium metal in 175 ml water and 25 ml 36N H_2SO_4. Heat in a boiling water bath until the metal is dissolved. Cool and dilute to 250 ml with water. Prepare fresh daily.

2) Dithiol Reagent: Dissolve 1g toluene -3, 4-dithiol in 250 ml 0.25N sodium hydroxide. Add 1 ml thioglycolic acid. Prepare fresh daily.

3) Nitric acid, concentrated, HNO_3, 16N.

4) Hydrofluoric acid, HF, 27N.

5) Hydrochloric acid, HCl, 12N.

6) Sulfuric acid, H_2SO_4, 18N.

7) Nitric acid, dilute, 2N.

8) Carbon tetrachloride, CCl_4, Reagent Grade.

d. Procedure

Lithium samples containing the tungsten solute were received in Cb-1% Zr collectors. The lithium was dissolved from the collectors with water as is described in Section 9. The collector was rinsed with hot 2N HNO_3 and water, and the rinse solutions were combined with the metal dissolution solution and diluted to 100 ml.

Add 5 ml of sulfuric acid to an aliquot of the sample and evaporate to dense white fumes. Add 10 drops of concentrated nitric acid and again fume the sample. Add the following reagents in order and with mixing after each addition: 25 ml $Ti_2(SO_4)_3$; 20 ml hydrochloric acid, and 10 drops hydrofluoric acid. Heat the samples in a water bath (80-90°) for five minutes. Add 10 ml dithiol reagent and 10 drops of HF. Cool, transfer to a separatory funnel using 10 ml of CCl_4, and extract for two minutes. Transfer the organic phase to a 25 ml volumetric flask and repeat the extraction using 5 ml CCl_4. Read the samples against carbon tetrachloride in 5 cm path length absorption cells at 640 nm.

e. Discussion

It was determined experimentally that lithium at the 200 mg level and niobium at the 1000 µg level had no effect on the determination of tungsten by the dithiol procedure. The procedure is essentially that of Hobart and Hurley (10).

14. DETERMINATION OF RHENIUM IN LITHIUM

a. Principle

The determination of rhenium in lithium is based on the formation of the purple rhenium-furil dioxime complex. The rhenium-furil dioxime complex is formed by reducing the perrhenate with stannous chloride in the presence of an excess of the furil dioxime reagent. The complex is separated for analysis by a chloroform extraction.

b. Apparatus

Beckman Spectrophotometer, Model DU.

c. Reagents

1) Furil dioxime: Dissolve 0.8g furil dioxime in 100 ml absolute ethanol. Prepare fresh directly before use. Furil dioxime obtained from Eastman Organic Chemicals was used without purification.

2) Stannous chloride, $SnCl_2$, 10%. Dissolve 10g $SnCl_2$ in 10 ml concentrated HCl and dilute to 100 ml with H_2O.

3) Hydrochloric acid, HCl, concentrated, 12M.

4) Hydrochloric acid, HCl, dilute, 0.9M.

5) Nitric acid, HNO_3, 6M.

6) Formic acid, Reagent Grade.

7) Sodium Hydroxide, NaoH, 10%.

8) Ethanol, absolute, Reagent Grade.

9) Chloroform, $CHCl_3$, Reagent Grade.

d. Procedure

Lithium samples containing the rhenium solute were received in Cb-1% Zr collectors. The lithium was dissolved from the collectors as is described in Section 9. The collectors were rinsed in sequence with water, hot $6\underline{M}$ HNO_3, and water. All of the solutions were combined and diluted to 100 ml.

Heat an aliquot of the lithium sample containing 0-10 µg Re twice with 5 ml of formic acid to remove the oxides of nitrogen. After the removal of the nitrates, neutralize the sample to a phenolphthalein end point with sodium hydroxide. Add 2 ml concentrated HCl and dilute to 30 ml with H_2O. Transfer the solution to a separatory funnel using dilute hydrochloric acid to rinse the beakers. Add 10 ml of furil dioxime with mixing, followed by 10 ml of stannous chloride. After mixing, allow the solution to stand for one hour. Extract the rhenium-furil dioxime complex into 10 ml of chloroform. Transfer the organic phase to a 25 ml volumetric flask and dilute to volume with ethanol. Read the samples on a spectrophotometer against a blank (15 ml C_2H_5OH + 10 ml $CHCl_3$) in 5 cm path length absorption cells, at 532 nm.

Obtain a calibration curve by treating 0-10 µg of rhenium in the same manner as described in the procedure.

e. Discussion

It was determined experimentally that nitrate and fluoride interfere with the rhenium color and cause low results. Tungsten was checked at a ratio of 20:1 to rhenium and was found to have no effect. As much as 300 mg of lithium and 1000 µg of niobium also showed no effect. Absolute ethanol proved to be a good solvent for the furil dioxime and it also acted to prevent the formation of emulsions that have a tendency to form in the extraction step.

A spectrophotometric scan was made on a Cary Recording spectrophotometer and it showed that the maximum absorption of the rhenium-furil dioxime complex lies between 535 and 515 nm. There appeared to be no other interference peaks in the presence of niobium and lithium.

There was some evidence that rhenium is lost in the fuming process in the absence of lithium. This was not fully investigated because the samples being analyzed in this laboratory always contained lithium.

The method described here was based on those reported by Meloche et al., (21) and Landrum and Henicksman (16).

APPENDIX B

Specifications and Performance Data for the High Temperature Solubility Test Furnace

The specifications which were sent to prospective fabricators of the required 1600°C test furnace are given below. The successful bidder was Centorr Associates, Inc., Suncook, New Hampshire.

1. The furnace must be capable of maintaining the test capsule at a temperature level of 1600°C.

2. The temperature gradient along the test capsule must be such that the ends are maintained within 2°C of the center. (The temperature level control point is a tungsten-rhenium thermocouple which is pressed against the capsule at the nominal mid-point of length of the capsule).

3. The furnace is to have a clam-shell design with one fixed part and one movable part which swings outward on a vertically mounted shaft to fully expose the interior of the furnace hot zone to allow removal of the capsule as described below. The movable part of the furnace shall be stable in both the fully closed and the fully open positions, i.e., the furnace door must not swing closed when open, nor open when closed.

4. The furnace will preferably have a water-cooled outer shell, that is, both the movable and the fixed parts must be cooled. Methods of cooling other than a direct water-cooling may be used, but in no case should any part of the outer furnace shell exceed 400°C during a 12-hour test exposure at 1600°C.

5. The furnace door shall be fitted with a suitable handle to allow its being opened with the manipulators which are a part of the existing vacuum chamber.

6. A cup or yoke in which the test capsules will be seated during testing must be provided. The ID of the cup must be 0.760 ± 0.005 inches, and there must be a 1/16-inch diameter hole drilled through on a diameter of the cup and 1/16 - 5/64 inch from the inner bottom of the cup. The cup in turn is supported by a refractory metal column whose other end is fastened to a horizontal shaft which passes through the furnace below the hot zone.

   The test capsule itself is 6 3/4 inches long and 3/4-inch in diameter, except in the region of the cap, which is one-inch in diameter and about one inch in length.

7. The horizontal shaft which supports the capsule during the test must be rotatable through 180° to allow the capsule to be swung forward out of the furnace after the movable half of the furnace has been swung aside. In addition to removing the capsule from the furnace, the capsule is inverted in this operation.

8. The horizontal shaft which supports the capsule shall also have a means of adjusting the position of the capsule in the hot zone of the furnace and must support the capsule during the test period so as to avoid its falling against the heating element.

9. The furnace shall be mounted on a support at an elevation such that the capsule can be swung outward and downward to become fully inverted beneath the furnace. If necessary, the existing base-plate in the vacuum chamber may be modified to accommodate this requirement. The use of a rapid quench on the test capsule cap is an important requirement of the test procedure.

10. The maximum length of the furnace heating element shall be twelve inches, and the element shall be made of tantalum strip, or the equivalent.

11. The diameter of the furnace heating element (which bounds the hot zone) shall be 1 1/2 inches.

12. The furnace shall be fitted with six (6) thermocouple assemblies. Means for pressing the thermocouple beads against the capsule must be provided.

13. The thermocouples shall be tungsten-5% rhenium vs tungsten-26% rhenium, and shall be 0.010 diameter wire or larger, and thirty (30) inches long, and shall be mounted in one or more vacuum feed-throughs which are themselves mounted on a type 304 stainless steel plate which is double O-ring sealed to one of the penetrations in the chamber wall.

14. Thermocouple insulation shall be provided and must be made of a very high purity grade of Al_2O_3 (or of a material of equivalent thermal stability) for use in the highest temperature regions of the furnace. In the cooler regions along the length of the thermocouple, any suitable ceramic insulation (such as beads) which will allow flexing of the thermocouples may be used.

15. All radiation shields and supports used in the furnace shall be made of tantalum or of tungsten.

16. The furnace shell may be made of any suitable material.

17. The furnace assembly shall be designed to operate within a chamber whose inner diameter is nominally 24 inches (which chamber has a 22 inch unobstructed diameter), and whose height is nominally 22 inches. By modifying the base plate and using the head space in the domed chamber lid, the total usable height can be increased to 26 inches in a 20 inch diameter.

18. The vacuum chamber has the following parts available for use for power leads, thermocouple leads and cooling water feed-throughs:

a. Three each, 4-inch diameter (clear area),

b. One each, 7-inch diameter (clear area),

c. One each, 3-inch diameter (clear area).

The furnace manufacturer shall provide all covers for ports actually used in the overall furnace assembly and appurtenances. Ports not so used need not have new covers. All new covers shall have a double O-ring seal with Viton-A O-ring material for the inner seal, and neoprene (or Viton-A) for the outer seal. A between-ring pump-out shall be provided terminating in a standard 1/8" pipe thread. The O-ring sizes to be used are:

Clear Diameter	O-Ring Size Viton-A	Neoprene	Bolt Circle Diameter	No. Bolts	OD Flange
3"	#2-236	#2-241	4.75"	4	6.00"
4"	#2-244	#2-250	6.00"	6	6.63"
7"	#2-443	#2-446	9.50"	8	10.50"

19. The vacuum chamber (without its pumping system) will be shipped to the furnace manufacturer's plant at AI expense. The furnace manufacturer must design the furnace, together with the necessary power lead, thermocouple, and cooling water feed-throughs, to fit and to operate within the chamber. The chamber and the furnace (suitably packaged) shall be shipped at the furnace manufacturer's expense to AI. The furnace shall then be set up at AI and its satisfactory performance demonstrated.

20. Satisfactory performance of the furnace shall consist of proof of the attainment of the temperature and temperature gradient requirements, and operation at 1600°C for 8 hrs while maintaining a vacuum level of 3×10^{-6} torr or lower. (The existing vacuum system uses a NRC 6-inch oil diffusion pump system having a liquid nitrogen baffle, a water baffle, and a Welch Model 1397 mechanical pump. Dow Corning pump fluid # 705 is used.)

21. Two complete heating elements are required as spares (three complete elements in all.)

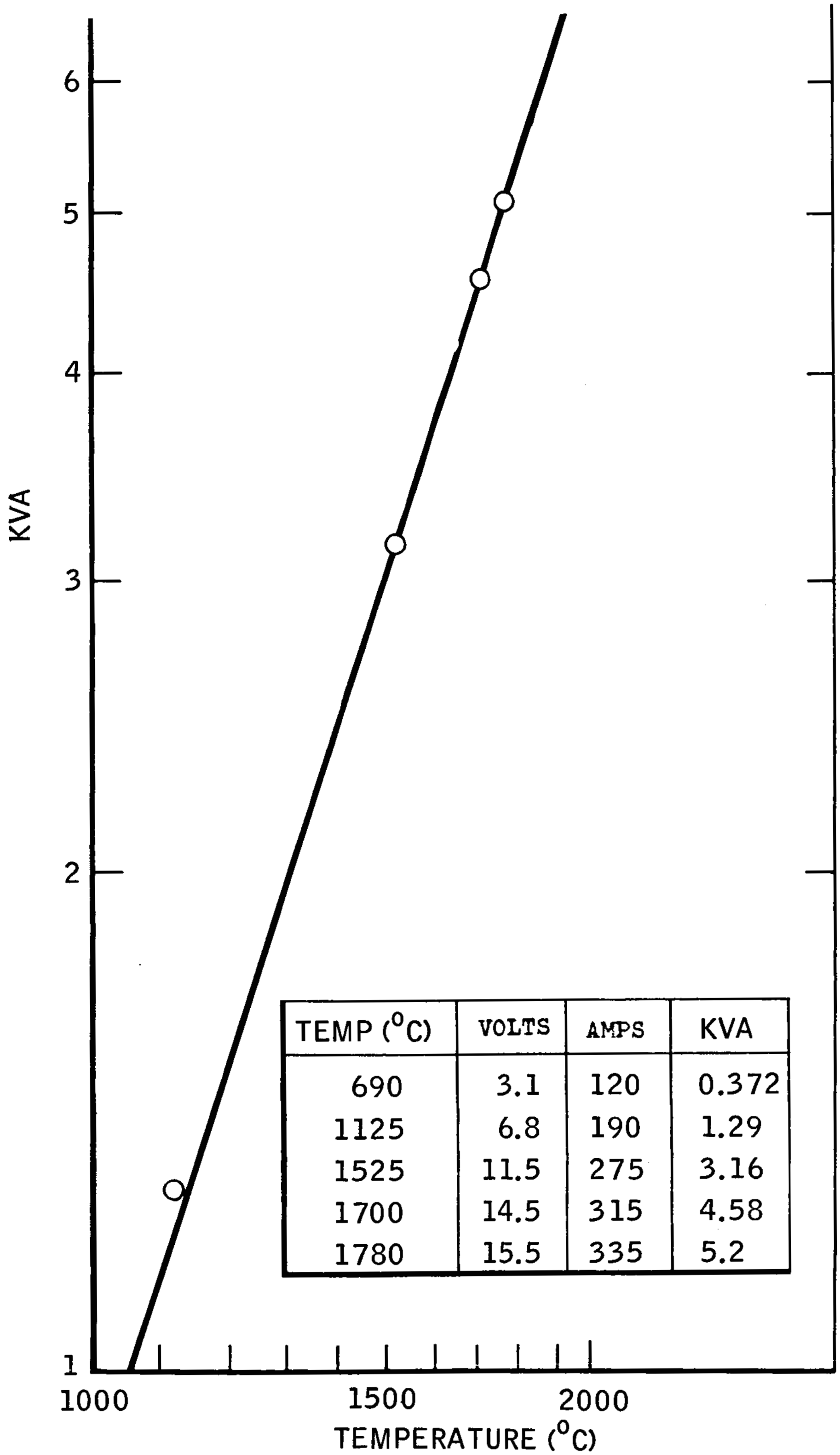
22. Four spare thermocouples are required (ten complete thermocouple-with-insulation sub-assemblies.)

23. The furnace shall be placed within the chamber to permit operation of the door and the capsule inversion operation to be performed with the existing manipulator.

24. Although these specifications describe a preferred furnace design, the proposer may offer an alternate design which satisfies the basic operational requirements of temperature, temperature gradient, capsule positioning in the furnace, and capsule inversion and quenching.

25. A step-down power transformer which is properly impedance matched and sized to the furnace heating element requirements shall be provided. The transformer must have a 220 v AC power input. Lead wires shall be provided to go from the secondary coil of the transformer to the furnace power feed-through. The maximum length of these leads is six feet. The estimated power requirement for 1600 °C operation shall be quoted in the response to this request for quotation.

The furnace input vs temperature data obtained by the manufacturer are shown graphically in Fig. 16.



TEMP (°C)	VOLTS	AMPS	KVA
690	3.1	120	0.372
1125	6.8	190	1.29
1525	11.5	275	3.16
1700	14.5	315	4.58
1780	15.5	335	5.2

Figure 16. High Temperature Furnace Input-Temperature Data.

APPENDIX C

Analyses of Solute, Collector, and Capsule Materials Used in Solubility Experiments

1. Solute Materials

T-111 Alloy (m.p. ~2980°C). Fansteel Lot # 11D1633

Element	Content (wppm)	Element	Content (wppm)
C	< 10	Nb	110
H	< 5	Cr	< 10
O	25	V	< 10
N	10	Co	< 10
Fe	20	W	7.87%
Ni	< 10	Hf	2.03%
Mo	100	Ta	balance

ASTAR-811C Alloy (m.p. ~ 3000°C). Supplied by NASA - Lewis Research Center, Cleveland, Ohio.

Nominal composition:

Element	Content, wt. %
W	8
Re	1
Hf	1
C	0.025
Ta	balance

Ta-0.5 Zr Alloy (m.p. ~ 2990°C). Fabricated by Westinghouse Astronuclear Laboratory from Fansteel raw materials.

Element	Content (wppm)	Element	Content (wppm)
C	10 - 20	Ca	< 5 ppm
O	15 - 24	Al	< 5 ppm
N	15 - 24	Cu	< 5 ppm
W	< 25 ppm	Sn	< 5 ppm
Nb	100 ppm	Cr	< 5 ppm
Mo	< 5 ppm	V	< 5 ppm
Ti	< 5 ppm	Co	< 5 ppm
Fe	< 10 ppm	Mg	< 5 ppm
Ni	< 5 ppm	Zr	0.46%
Si	< 5 ppm	Ta	balance
Mn	< 5 ppm		

Cb-1Zr Commercial Alloy (m.p. 2410°C). Haynes Alloy CB-751, heat # 5191.

Element	Content (wppm)
C	70
O	55
H	4
N	54
Zr	0.95%
Nb	balance

Nb-0.5 Zr Alloy (m.p. ~ 2400°C). Fabricated by Westinghouse Astronuclear Laboratory from Fansteel raw materials.

Element	Content (wppm)
C	16
O	65
N	50
Ta	250 ppm
Ti	< 50 ppm
Fe	< 50 ppm
W	< 100 ppm
Si	< 10 ppm
Mo	< 100 ppm
B	< 2 ppm
Zr	0.51%
Nb	balance

Mo-0.5 Zr Alloy (m.p. ~ 2600°C). Fabricated by Westinghouse Astronuclear Laboratory from Fansteel raw materials.

Element	Content (wppm)
C	12 - 15
O	15 - 31
N	15 - 34
W	< 200
Si	< 100
Ni	< 80
Fe	< 50
Others	< 50
Zr	0.51%
Mo	balance

Hafnium (m.p. 2130°C). Electron beam zone refined material fabricated by Materials Research Corporation.

Element	Content (wppm)	Element	Content (wppm)
C	< 80	Ta	< 100
O	< 100	Ti	< 20
N	< 16	V	< 5
Al	< 20	W	< 10
Co	< 5	B	< 0.2
Cu	< 30	Cd	< 2
Fe	140	Cr	20
Mg	< 5	Na	< 5
Mn	< 5	Pb	< 10
Mo	< 5	Ca	< 20
Nb	< 50	Sn	< 20
Ni	< 20	U	< 1
Si	< 20		

Zirconium (m.p. 1830°C). Electron beam zone refined material fabricated by Materials Research Corporation.

Element	Content (wppm)	Element	Content (wppm)
Li	< 0.001	Sr	< 0.05
Be	< 0.01	Y	< 0.15
B	0.005	Nb	< 0.5
C	6.0	Mo	< 0.6
N_2	2.1	Ru	< 0.6
O_2	125.0	Rh	< 0.2
F	< 0.1	Pd	< 0.8
H_2	3.3	Ag	< 0.4
Mg	< 0.05	Cd	< 0.5
Al	3.0	In	< 0.08
Si	1.5	Sn	< 0.25
P	0.1	Sb	< 0.15
Cl	2.0	Te	< 0.4
K	0.004	I	< 0.07
Ca	0.04	Cs	< 0.07
Ti	1.0	Ba	< 0.1
V	0.05	La	< 0.08
Cr	0.5	Ce	< 0.08
Mn	< 0.03	Pr	< 0.08
Fe	30.0	Nd	< 0.3
Co	< 0.007	Sm	< 0.06
Ni	1.5	Eu	< 0.04
Cu	0.01	Gd	< 0.07
Zn	< 0.5	Tb	< 0.02
Ga	< 0.02	Dy	< 0.06
Ge	< 0.03	Ho	< 0.02
As	< 0.01	Er	< 0.05
Se	< 0.01	Tm	< 0.02
Br	< 0.02	Yb	< 0.1
Rb	< 0.02	Lu	< 0.01

Element	Content (wppm)	Element	Content (wppm)
Hf	< 40.0	Au	< 0.2
Ta	0.2	Hg	< 0.7
W	< 0.7	Tl	< 0.012
Re	< 0.3	Pb	< 0.015
Os	< 0.4	Bi	< 0.007
Ir	< 0.03	Th	< 0.008
Pt	< 0.2	U	< 0.05

Rhenium (m.p. 3170 °C). Solute crucible fabricated by Chase Brass and Copper Co., Inc., from sheet stock, lot #RS-58.

Element	Content (wppm)
Al	< 1
Ca	< 1
Cr	< 1
Cu	< 1
Fe	42
Mg	< 1
Mo	30
Na	< 1
Ni	< 1
Si	< 1
W	not detected

TZM Commercial Alloy (m.p. 2610 °C). A specific analysis of the TZM used as solute is not available. Impurity levels are expected to be consistent with those reported for the other refractory metal alloys used. Nominal composition of the alloy and maximum impurity content are given below.

Element	Nominal Content (wt.%)
Ti	0.5
Zr	0.07
C	0.03
Mo	balance

Impurities	max. wppm	Impurities	max. wppm
O	20	Al	20
N	10	Ca	20
H	5	Mn	20
W	120	Mg	20
Si	80	Co	20
Fe	80	Pb	10
Cr	25	Ta	100
Sn	40	Nb	100
Ni	20	V	100
Cu	20		

Tungsten (m.p. 3380 °C). Tungsten crucibles were fabricated at Atomics International by a vapor deposition process which involves the hydrogen reduction WF_6 on a heated stainless steel mandrel.

2. Collector Materials

Mo-1/2 Ti (m.p. 2610 °C). Fabricated by General Electric Company Refractory Metals Plant for Northwest Industries, Inc.

Element	Content (wppm)	Element	Content (wppm)
C	160	Cu	not detected
O	24	Mn	< 10
H	1	Mg	60
N	25	Sn	not detected
Al	40	Co	"
Ca	50	Ag	"
Si	35	Pb	"
W	40	Zr	"
Fe	15		
Cr	< 10	Ti	0.50%
Ni	10	Mo	balance

Cb-1 Zr (m.p. 2410 °C). Haynes Alloy Cb-751, fabricated by Union Carbide Corp., Stellite Division.

Element	Content (wppm)
C	70
O	55
H	4
N	54
Zr	0.95%
Nb	balance

3. Capsule Materials

Molybdenum (m.p. 2625 °C). Molybdenum capsule bodies and caps were fabricated for a previous project (Reference (20)) from rods of arcmelted molybdenum. Its nominal purity was quoted to be 99.9+%. The certified impurity levels are: O_2 < 3 ppm; H_2, < 1 ppm; C, 140 ppm; N_2, 9 ppm; Ni, < 10 ppm; Fe, < 10 ppm; and Si, < 10 ppm. The machining of the capsules and caps was done using chlorethene as a lubricant because it has been found to contaminate the metal surface less than other machining lubricants.

T-222 Alloy (m.p. ~ 3030 °C). Capsule bodies and caps of T-222 were fabricated by Wah Chang Corporation. The analysis given is for the ingot from which the capsule bodies were made, heat # 65032.

Ingot Analysis, Composition, %

	Top	Bottom
W	9.4	9.4
Hf	2.70	2.0
Ta	balance	

Ingot Impurities, wppm

	Top	Bottom
C	140	130
H	2.6	1.9
N	17	17
O	< 50	< 50
Al	< 10	< 10
Cb	<300	<300
Co	< 5	< 5
Cr	< 10	< 10
Cu	< 20	< 20
Fe	< 20	20
Mo	< 10	< 10
Ni	< 10	< 10
Si	20	20
Ti	< 20	< 20
V	40	15

APPENDIX D

STATISTICAL TREATMENT OF TANTALUM ANALYSIS

The statistical treatment of the data obtained in analytical procedures development studies described **previously** is discussed below. The data used were those obtained from "sample" solutions containing (1) tantalum only, (2) tantalum plus molybdenum, (3) tantalum plus lithium, and (4) tantalum plus molybdenum plus lithium.

Equations for the regression curves are as follows:

(1)	Ta alone:	$\hat{y} = -0.010137 + 0.015676x$	$N = 16$
(2)	Ta + Mo:	$\hat{y} = -0.013095 + 0.017948x$	$N = 15$
(3)	Ta + Li:	$\hat{y} = -0.006615 + 0.01623x$	$N = 14$
(4)	Ta + Mo + Li:	$\hat{y} = -0.013516 + 0.018228x$	$N = 24$
	Pooled:	$\hat{y} = -0.010639 + 0.0170689x$	$N = 69$

where x is micrograms of tantalum, $\hat{y}$ is the optical density estimated from the regression relationship, and N is the number of observations.

The sum of the squares of the deviations from the best line drawn through each set of data separately ($\Sigma\Sigma'\hat{y}^2$) represents the minimum deviation which can be obtained by a straight line correlation and was used as an error estimate for testing the significance of other deviations. The sum of the squares of deviations from the best line through the means of the sets of data ($\Sigma'\hat{y}_m^2$) is a measure of any trend from one set of data to the next. $\Sigma'\hat{y}_w^2$ is the sum of squares of deviations from separate lines drawn through each set of data, but all drawn with the same slope, while $\Sigma'\hat{y}^2$ is the sum of squares of deviations from the best line through all the data. Using this symbolism, the analysis of variance can be summarized as shown in Table XXX.

Table XXX

ANALYSIS OF VARIANCE

		DF	Sum of Squares	Mean Square
Means Correlation	$\Sigma'\hat{y}_m^2$	$(K-2) = 2$	0.0012367	0.00061835
Difference between means slope and pooled slope	$\Sigma'\hat{y}^2 - \Sigma'\hat{y}_m^2 - \Sigma'\hat{y}_w^2$	1	0.000171	0.000171
Between slope	$\Sigma'\hat{y}_w^2 - \Sigma\Sigma'\hat{y}^2$	$(K-1) = 3$	0.000565	0.000188
Error	$\Sigma\Sigma'\hat{y}^2$	$\Sigma(n_i-2) = 61$	0.004651	0.000076245
Total	$\Sigma'\hat{y}^2$	$N-2 = 67$	0.0066237	

Mean Squares Ratios:

Between Slopes/Error $= 188/76.245 = 2.4657$

$F\binom{3}{61}$ 0.01 = 4.13
0.05 = 2.76
0.10 = 2.18

Difference/Error $= 171/76.245 = 2.2428$

$F\binom{1}{61}$ 0.10 = 2.79
0.25 = 1.35

Means/Error $= \dfrac{6183.5}{762.45} \equiv 8.11$

$F\binom{2}{61}$ 0.005 = 5.80

The ratio of the "between slopes" mean square and the "error" mean square of 188/76.245 = 2.466 were tested against F at 3 and 61 degrees of freedom. The F values are 2.18 at the 0.10 level and 2.76 at the 0.05 level indicating that the amount of deviation removed by using individual least-squares lines for each set compared to that removed by using a pooled slope for all sets is slightly significant. There is less than 10 per cent and more than 5 per cent chance of being in error if the lines are considered not to have a common slope.

The ratio of the "difference" mean square to the "error" mean square of 171/76.245 = 2.243 appears to be of no statistically valid significance.

The ratio of the "means" mean square and the "error" mean square of 8.11 is very highly significant. There is less than 0.1 percent chance of being in error when comparing the amount of deviation removed by a line through the means of the sets of data with the minimum deviation attainable and rejecting the hypothesis of equal variances, showing there is some trend from one set to another.

By use of Student's t test, the means of the individual sets can be compared to the mean of tantalum alone, as follows:

Set	t calculated (D.F.)	Significance
Ta + Li	0.507(26)	no significant difference
Ta + Mo	2.385(27)	$t_{.025} < t\ \text{calc} < t_{.01}$
Ta + Mo + Li	2.395(35)	$t_{.025} < t\ \text{calc} < t_{.01}$

These data appear to indicate the presence of Mo to be statistically significant in the determination of Ta. The practical extent of this difference was investigated. Using the pooled data, the variance of a single estimated value (Y_i) was calculated and the 95 percent confidence limits for a measurement at 2 μg and 10 μg Ta were determined. A similar value was calculated for the Ta + Mo + Li set. These values were found to be indistinguishable from each other. The value for the uncertainty in Y_i is equivalent to ± 1.2 μg (95% confidence level).

An earlier observation that the slope of the extracted Ta curve was about 85 percent of that of the unextracted curve gives rise to a suspicion of incomplete extraction. Use of a radioactive tracer (^{182}Ta) indicated that 98 percent was recovered in the extract.

LITERATURE CITED

1. R. Belcher, T. V. Ramakrishna, and T. S. West, "Absorptiometric Determination of Niobium with 4-(2-pyridylazo)-Resorcinol as Reagent," Talanta 13, 689 (1966)

2. N. M. Beskorovaynyy and Yu. I. Yakovlov, "Study of Corrosion of Iron and Chromium Steels in Liquid Lithium," Metallurgy and Metallography of Pure Metals (Translation) Gordon and Breach, N. Y. (1962)

3. S. S. Blecherman, G. F. Schenk, and R. E. Cleary, "Solubility Studies in Alkali Metals," CONF-650411-4 (1965); also CNLM-6335

4. Yu. F. Bychkov, et al., "Determination of Solubility of Metals in Lithium," Met. i Metalloved. Christykh Metal, Sbornik Nauch. Rabot (1960) (2), 178 CA:55:15281c (1961)

5. Yu. F. Bychkov, et al., "Determination of the Solubility of Metals in Lithium," Soviet J. Atomic Energy 7, 987 (1959)

6. Yu. F. Bychkov, et al., "Determining Solubility of Metals in Lithium," Metallurgy and Metallography of Pure Metals, Translation by B. Chalmers, Gordon and Breach Publ., N. Y. (1962)

7. J. P. Coughlin, "Contributions to the Data on Theoretical Metallurgy, XII. Heats and Free Energies of Formation of Inorganic Oxides," U.S. Bureau of Mines Bulletin 542 (1954)

8. W. S. Ginell and R. J. Teitel, "Determination of the Solubility of Transition Metals in Molten Potassium," SM-48883 (1965)

9. J. H. Hill, "Spectrophotometric Determination of Trace Amounts of Tantalum," Analyst 91, 659 (1966)

10. E. W. Hobart and E. P. Hurley, "Spectrophotometric Determination of Molybdenum and Tungsten in Niobium with Dithiol," Anal. Chim. Acta 27, 144 (1962)

11. E. E. Hoffman, "Corrosion of Materials by Lithium at Elevated Temperatures, ORNL-2924 (1960)

12. JANAF Thermochemical Tables, Clearinghouse for Federal Scientific and Technical Information, PB 168 370 (August, 1965)

13. D. S. Jesseman, et al., "Preliminary Investigation of Metallic Elements in Molten Lithium," NEPA-1465 (1950)

14. K. J. Kelly, "Liquid Metal Corrosion Research," NASA-AEC Liquid Metals Corrosion Meeting, Dec. 7-8 (1960), Washington, D.C., NASA-TN-D-769, p. 27 (1961)

15. R. F. Koenig, "Corrosion of Zirconium and Its Alloys in Liquid Metals," KAPL-982 (1953)

16. J. H. Landrum and A. L. Henicksman, "The Separation of Rhenium from Copper, Molybdenum, and Tungsten, and Its Spectrophotometric Determination," LA-3550 (1966)

17. H. W. Leavenworth and R. E. Cleary, "Solubility of Ni, Cr, Fe, Ti, and Mo in Liquid Lithium," Acta. Met. 9, 519 (1961); (PWAC-356)

18. C. L. Luke, Photometric Determination of Tantalum with Phenylfluorone," Anal. Chem. 31, 904 (1959)

19. A. S. L'vova and N. N. Feodosev, "Enthalpy of Formation of Lithium Metahafnate," Chemical Abstracts 63:17222e (Zh. Neorgan. Khim. 10 (10), 2378 (1965) (Russ.)

20. R. L. McKisson, R. L. Eichelberger, R. C. Dahleen, J. M. Scarborough, and G. R. Argue, "Solubility Studies of Ultra-Pure Transition Elements in Ultra-Pure Alkali Metals. Final Report," AI-65-210 (1965); also NASA-CR-610

21. F. W. Meloche, R. L. Martin, and W. H. Webb, "Spectrophotometric Determination of Rhenium with Alpha-Furildioxime," Anal. Chem. 29, 527 (1957)

22. T. Nelson, C. Moss, and L. G. Hepler, "Thermochemistry of Potassium Chlorate, Potassium Molybdate, Potassium Chlorate, Sodium Chlorate, Sodium Chromate, and Sodium Dichromate," J. Phys. Chem. 64, 376 (1960)

23. E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, Inc. (1959)

24. D. R. Stull and G. C. Sinke, Thermodynamic Properties of the Elements, Advances in Chemistry Series, #18, American Chemical Society, Washington, D. C. (1956)

25. J. H. Swisher, "Solubility of Iron, Nickel, and Cobalt in Liquid Potassium and Effect of Oxygen Gettering Agents on Iron Solubility," NASA-TN-D-2734 (1965)

26. N. S. Thien and L. A. Zharkova, "Heat of Formation of Lithium Molybdate" Chemical Abstracts 65:9827d (Zh. Fiz. Khim. 40 (6), 1370 (1966) (Russ.)

27. D. D. Williams, J. A. Grand, and R. R. Miller, "Determination of the Solubility of Oxygen Bearing Impurities in Sodium, Potassium, and their Alloys," J. Phys. Chem. 63, 68 (1959)

28. D. F. Wood and J. T. Jones, "Determination of Zirconium and Hafnium in Niobium and Other Methods with Catechol Violet," Analyst 90, 125, March (1965)

29. J. P. Young and J. C. White, "The Extraction of Zirconium with Tri n-octyl Phosphine Oxide and Its Direct Determination in the Organic Phase with Pyrocatechol Violet," Talanta 1, 263 (1958)

NASA-Langley, 1969 —— 17 E-4961